STEELCASE FINAL REPORT

Greener Solutions, UC Berkeley

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Introduction

The Challenge: Plastics and Downcycling

Plastic-containing products largely end up as waste at the end of their useful life. The United States produced over 32 million tons of plastic in 2013, 75% of which ended up in landfills (US EPA, 2015). Plastic in landfills and the environment can persist for hundreds of years without degrading. This can create physical and toxicological hazards for humans and other living organisms. Only 9.5% of the plastic produced in the U.S. during 2013 was recovered for recycling (US EPA, 2015). There are both economic and technological barriers to effectively recycling plastics, and this report is focused on the latter.

The small percentage of plastic that is recycled is not returned to its initial state and quality because of the enormous diversity of plastic produced. There are many different plastic resins in circulation, which can be identified by the resin identification code numbers 1 through 7. Each plastic resin has its own unique material properties ideally suited for a specific application. These resins are often incompatible with each other, and therefore the first step in the recycling process is to sort the collected plastic by the dominant resin. The sorting procedure can be very resource-intensive and include many different stages. In addition, many products, such as office furniture, have individual parts made from different types of plastic that must be physically separated and then sorted.

Once the recycled plastic is sorted by the dominant resin, it is chipped into very small pieces and then melted and formed into pellets that can be sold to manufacturers. However, the resulting pellets contain all the different additives present in the collected plastic, such as flame retardants, plasticizers, and colorants. Additives are necessary for imparting certain properties when products are manufactured and used, but at the end of the product's life they present a significant barrier to recycling. The recycled plastic lacks the purity necessary to match the original manufacturing process. For example, with colorants, plastic resins of the same type but different colors are chipped and melted down together. This amalgamation of colors only allows for dark brown or black recycled plastics. Thus, plastics are currently never truly recycled; they are 'downcycled' to much lower quality mixtures than the initial pure plastic resins due to contamination from many different additives.

The end of life problems with plastics demonstrate the need to change the way plastics are produced and processed. The concept of a circular economy for plastics encompasses this necessary transformation. Circular economy refers to an industrial production process that is designed to minimize waste and pollution by restoring and regenerating high-quality products and materials. Two types of materials can be incorporated into a circular economy: bio-based

materials that degrade readily and safely, such as biodegradable plastic, and high-quality technical materials that can exist in closed loop of use and reuse, such as recyclable plastic (Stahel, 2016). Motivated by recycling challenges and the goals of Steelcase we have focused our research on the latter option – developing truly recyclable plastics.

Steelcase's Plastic Vision: Polymer Modularity

Steelcase is the largest office furniture manufacturer in the world (Steelcase, 2016). The prospect of true recycling is a tantalizing prospect for major users of plastic like Steelcase. True recycling reduces the need for new material and reduces hazards associated with plastic in the environment. Steelcase envisions a solution to plastic recycling that would produce a circular economy for plastics. They have proposed the concept of "polymer modularity", which would reduce the need for many different plastics by embedding a wider range of properties in just a few polymers. These properties would be imparted by modifying the polymer backbone to bind additives, rather than using free-flowing additives within the polymer matrix. For example, Trevira CS is a flame-retardant textile with the flame retardant attached directly to the polyester fiber (Trevira, 2016).

Altogether, the removal of free-flowing additives and reduction of the number of resin waste streams could greatly improve the recycling of plastic. With additional advances in polymer chemistry, instead of chipping the plastic and melting it, the modular polymers could be depolymerized into its monomer units, sorted, and then repolymerized. In theory, this recycling process produces a polymer resin that can be used to recreate high value plastic goods. Polymer modularity represents one technical pathway towards the circular economy and more sustainable use of products.

While commercializing this process is not feasible in the near-term, polymer modularity is a long-term vision, reflecting Steelcase's more than 100 years of history and its powerful role in the market.

Project Scope

The concept of polymer modularity requires rethinking both the manufacturing and recycling of plastics. The scope of this project focuses on one area of the current plastic manufacturing process that would require changes to execute polymer modularity — additives. With polymer modularity, any additives to the polymer resin will be directly bound to the polymer backbone, whereas current additives are free-flowing within the polymer matrix. To begin investigating technical approaches to polymer modularity, we further focused the scope of this project from all possible additives to colorants. Colorants are an especially important additive because the property that they impart is visible to the consumer, and the first impression of the quality of the

product is tied to its appearance. High quality products are expected to be uniformly colored with vivid hues. ***Thus, our project goal is to identify strategies that impart color to a polymer without the use of a free-flowing additive.*** The model system for our work with Steelcase is the Node chair seat shell, which comes in over 20 different colors.

Current Manufacturing Process

Although Steelcase is not a polymer or a plastic molding company, it has the ability to influence its supply chain through product manufacturing specifications. The manufacturing of the Node chair seat shell is carried out by a tiered structure of suppliers, as outlined in Fig. 1. The Node chair seat shell is made from 100% polypropylene (PP) with a polyethylene random copolymer. A liquid masterbatch, which contains all of the necessary additives including the colorant, is added to the pure polymer pellets during injection molding. The injection molding procedure melts the pellets at a high temperature and injects the material into a mold of the chair. When the polymer cools, all of the additives are dispersed within the polymer matrix. This process relies on freely flowing additives to impart non-inherent properties to the plastic.

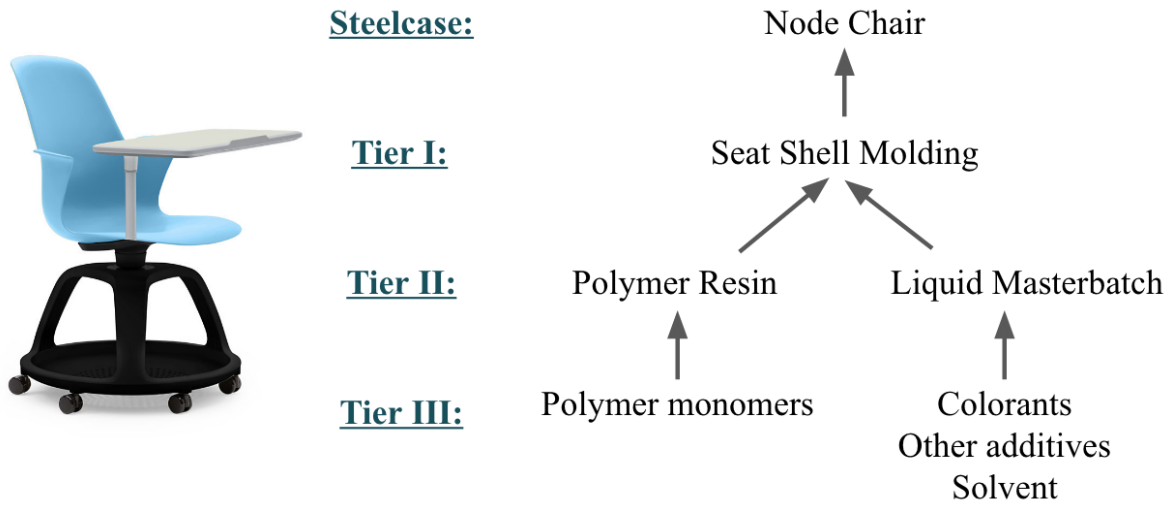

Figure 1. Manufacturing process for the Node chair seat shell

Methods

Strategy Identification

Our goal for Steelcase is to develop viable strategies for polymer modularity while also ensuring that these strategies align with Steelcase's sustainability goals. We identified strategies by using our conversations with Steelcase to inform a literature review on binding additives, specifically pigments, to polypropylene. We also interviewed polymer and manufacturing experts to validate our proposed strategies and identify new ones.

Hazard Assessment

To align with Steelcase's sustainability goals, we needed to characterize the hazards associated with Steelcase's current manufacturing process and our proposed strategies for polymer modularity. We did this through a systematic three step process shown in Fig. 2.

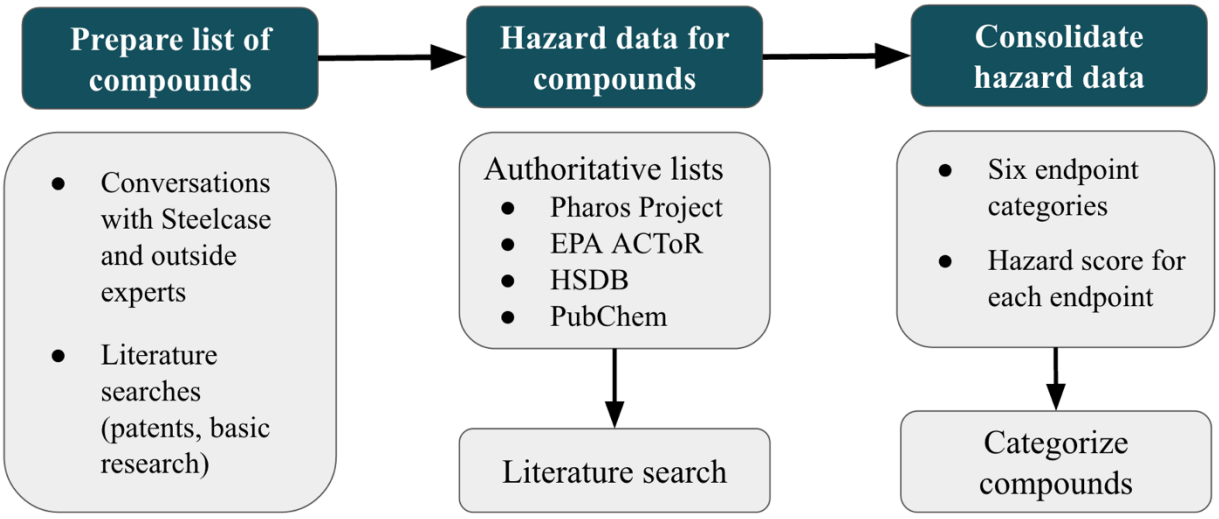

Figure 2. Hazard assessment workflow

First, we generated a list of compounds for the current manufacturing process and for our alternative strategies. Conversations with Steelcase and outside experts as well as literature searches helped identify the most salient compounds for further analysis. Once we had a complete list of chemicals for each strategy we began our hazard analysis.

We first collected hazard data from authoritative lists (e.g. GHS, MAK, German FEA, Canada domestic substances list, REACH) compiled by the Pharos Project (https://www.pharosproject.net/). We then searched EPA ACToR

(https://actor.epa.gov/actor/home.xhtml), Hazardous Substances Data Bank (https://toxnet.nlm.nih.gov/newtoxnet/hsdb.htm), PubChem (https://pubchem.ncbi.nlm.nih.gov/), and material safety data sheets for additional information. These data banks provided authoritative list information, experimental results, and predicted toxicological properties. If hazard information was lacking for a particular compound or endpoint, we then performed a primary literature search to fill in data gaps to the best of our ability. The complete hazard information for each compound can be found in Appendix I.

We consolidated the hazard information for each compound into a hazard table to make the data easily understandable and comparable. We chose six categories of hazard endpoints that were of particular concern to Steelcase and were important for early stage screening of health and environmental impacts. Table 1 shows the endpoint categories along with the hazard scale for each of these categories. We gave each chemical a hazard ranking on a scale of 1-4 representing least (1) to most (4) hazardous for each endpoint category. This ranking was based on criteria and language adapted from authoritative lists such as the International Agency for Research on Cancer (IARC) monograph. Details on each ranking can be found in Appendix I.

Table 1. Hazard assessment rubric

	4	**3**	**2**	**1**
Carcinogenicity / Mutagenicity	Known	Suspected	Possible	Probably not
Reproductive / Developmental Toxicity	Known	Suspected	Possible	Probably not
Sensitization	Known respiratory and skin sensitizer	Suspected resp. and known skin	Suspected skin	Probably not
Persistence / Bioaccumulation	Very persistent and bioaccumulative	Very persistent	Moderately persistent and bioacc.	Low persistence and bioaccumulation
Environmental Toxicity	Very high	High	Moderate	Low
Acute Toxicity	Very high	High	Moderate	Low

Our hazard search focused only on the properties of the chemicals themselves, not on risk or exposure during the manufacturing, use, or recycling phase. If Steelcase is interested in pursuing

these strategies, we suggest that they conduct full Green Screen hazard assessments for the chemicals they anticipate using, taking into account the chemical characteristics that drive exposure.

Current Manufacturing Hazards

We applied our hazard assessment methodology to the current manufacturing process for the Node chair seat shell. Table 2 shows the hazard assessment for several of the current pigments used to color the Node chair seat shell. This list of pigments is not exhaustive but does cover many of the common classes currently used, including halogenated (phthalocyanine green, pigment red 254, pigment yellow 191) and metal pigments (chromium oxide, titanium dioxide). There were varying amounts of hazard data available for these pigments. The metal pigments and carbon black had readily available hazard data through authoritative lists. The halogenated pigments had considerably less information as evidenced by the data gaps for reproductive or developmental toxicity.

We also completed a hazard assessment on the two polymers that make up the plastic of the Node chair seat shell. The hazard summary is in Table 3 with more data in Appendix I. The hazards of the monomers used to make the polymer were not assessed for this report. Monomer hazards are important for occupational workers as well as users if they remain trapped within the polymerized product. Both polypropylene and polyethylene have very similar hazards. Neither polymer is carcinogenic and both polymers have data gaps for reproductive and developmental toxicity. Both polymers are considered sensitizers because they can chip into very small pieces that when inhaled can cause asthma. Both polymers are also persistent and not biodegradable.

Although this report does not investigate alternative polymers, we present this information as a starting point for considering polymers for the full implementation of polymer modularity. Understanding the hazards associated with the current manufacturing process gave us a baseline to compare our strategies against. It also showed us certain areas of the current manufacturing process that could be optimized by replacing a hazardous substance with a less hazardous alternative.

Table 2. Hazard assessment for current colorants

Less Hazardous → More Hazardous (1 → 4)	Phthalocyanine Green	Pigment Red 254	Pigment Yellow 191	Chromium Oxide	Titanium Dioxide	Carbon Black
Carcinogenicity / Mutagenicity	1	3	3	2	4	4
Reproductive / Developmental Toxicity	No data	No data	No data	1	No data	3
Sensitization	No data	2	2	4	3	3
Persistence / Bioaccumulation	3	1	4	2	2	3
Environmental Toxicity	1	2	4	4	2	1
Acute Toxicity	2	No data	2	4	3	4

Table 3. Hazard assessment for current polymers

Less Hazardous → More Hazardous (1 → 4)	Polypropylene	Polyethylene
Carcinogenicity / Mutagenicity	1	1
Reproductive / Developmental Toxicity	No data	No data
Sensitization	3	3
Persistence / Bioaccumulation	2	2

Environmental Toxicity	**1**	**3**
Acute Toxicity	**2**	**2**

Feasibility Assessment

In addition to characterizing hazards, we also assessed the feasibility for each strategy presented in this report. This assessment was based on each strategy's ability to meet the performance criteria set by Steelcase. Quantitative properties include the melt flow rate, tensile strength and impact strength of the final product given in Table 4. These criteria were provided in conversations with experts at Steelcase. It is also important that any additive, including colorants, survive the molding temperature of 200-300 C.

Table 4. Quantitative Performance Constraints

Performance constraints for the Node chair seat shell	
Melt flow (230 C, 2.16 kg)	12.0 g/10ft
Tensile strength at yield (2 in/min)	4,300 PSI
Notched Izod Impact Strength at 23 C	1.1 ft・lb/in

There are also qualitative performance criteria such as uniform color distribution and saturation. We have structured our strategies for polymer modularity based on these feasibility and consumer considerations.

Strategies for Steelcase

Our strategies are divided into two categories. The first category addresses the problem posed by current hazardous colorants by suggesting less hazardous alternatives. This strategy would require minimal alteration to the current manufacturing process, and thus is a more near-term strategy. The second category directly addresses the goal of polymer modularity. All of the strategies in this category – grafting polypropylene, maleated polypropylene, and polypropylene binding peptides – bind colorants to the polypropylene backbone. These strategies require alterations to the current manufacturing and recycling processes and thus are longer-term strategies. Fig. 3 summarizes our strategies by type, and organizes them on a timeline of near- to long-term implementation.

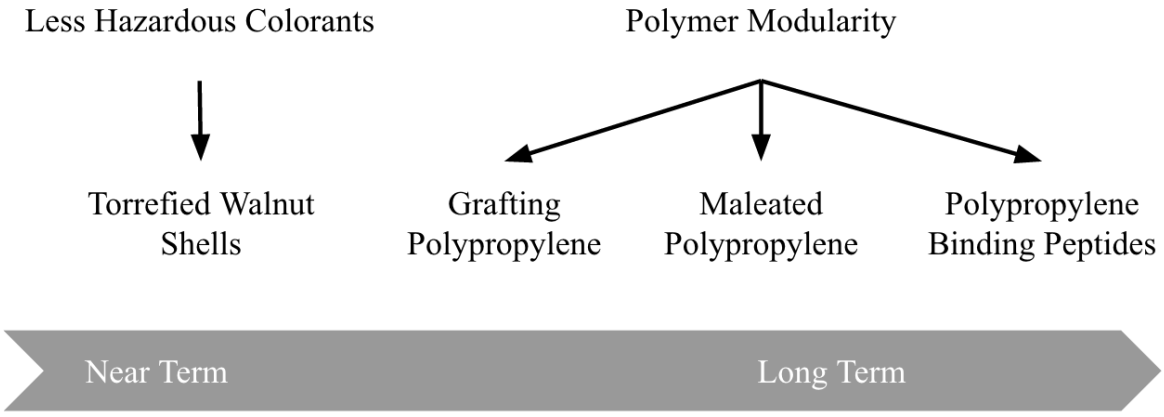

Figure 3. Timeline for strategies for polymer modularity and less hazardous colorants

Less Hazardous Pigments

Torrefied Walnut Shells

Our first strategy focuses on finding safer alternatives to pigments currently used to color the Node chair seat shell. One of the most hazardous colorants currently used is carbon black. This pigment is ubiquitous in manufacturing colored polymer products and is a well-known occupational hazard and probable carcinogen. Therefore, we have focused on an alternative to carbon black for this strategy.

Walnut shells are an agricultural waste product that can be torrefied to produce a pigment that ranges in color from brown to black. Torrefication of biomass is a technically proven process, but is not yet commercialized. Torrefication refers to heating the biomass at 200-300 C under nitrogen so that it cannot oxidize. At the high temperature, many biomolecules decompose leaving only cellulose and lignin biopolymers. Torreficiation of biomass has mostly been investigated as a potential biomass-to-energy pathway, although there can be other commercial applications of the final product, including as a filler and a pigment (Tumuluru, 2011).

Hazards

We assessed the hazards for lignin and cellulose, the primary compounds left in torrefied walnut shells. The hazard data is presented in comparison with carbon black in Table 5. Lignin and cellulose are generally less hazardous than carbon black, but there are hazard data gaps. These substances are perceived as not hazardous since they are present in all plant tissue and are a part of the human diet. In fact, lignin has been researched as a beneficial compound (Anderson, 2009; Baurhoo, 2008) and cellulose is exempt from the EU REACH database due to intrinsic safety. There are some toxicity hazards associated with cellulose, likely due to physical form, as very small particles or fibers can be inhaled.

Table 5. Hazard assessment for torrefied walnut shells

Less Hazardous (1) → More Hazardous (4)	Carbon Black	Lignin	Cellulose
Carcinogenicity / Mutagenicity	**4**	**No data**	**1**
Reproductive / Developmental Toxicity	**3**	**No data**	**No data**
Sensitization	**3**	**No data**	**No data**
Persistence / Bioaccumulation	**3**	**1**	**1**
Environmental Toxicity	**1**	**1**	**1**
Acute Toxicity	**4**	**2**	**2**

Feasibility

Torrefied walnut shells must survive the manufacturing process for the Node chair seat shell to be a viable replacement for carbon black. The torrefication process occurs at temperatures similar to the molding temperature, therefore we expect the torrefied walnut shells to survive injection molding. Prior laboratory research at USDA has demonstrated that the torrefied walnut shells can impart brown and black color in a plastic polymer. These are promising results for the overall feasibility of this strategy, though more testing is needed to determine the mechanical properties of the Node chair seat shell with this new pigment.

Torrefied walnut shells are a promising strategy for reducing the hazards associated with carbon black with minimal changes to the current manufacturing process. Other biomass waste products can also be considered for torrefication to produce brown and black pigment. The re-use of agricultural waste as high-quality pigment would also demonstrate circular economy principles. We recommend that, if interested in this strategy, Steelcase can contact the researchers who have

successfully created plastic colored with torrefied walnut shells and discuss potential performance impacts.

Bonding Colorants to Polypropylene

Polymer modularity aims to reduce the number of different polymers by binding additives directly to the polymer backbone. The following three strategies focus on methods for binding additives to the polymer backbone, specifically binding colorants to polypropylene. Polypropylene presents its own set of challenges because it is essentially inert. The backbone of polypropylene contains only carbon – carbon and carbon – hydrogen bonds, which are very difficult to break or react with. Given the difficulty of binding to polypropylene, it may not be the top contender for implementing the grand scheme of polymer modularity. However, this report focuses on polypropylene because it is the main material of the Node chair seat shell.

Grafting Polypropylene

Grafting polypropylene is a technique to directly bind molecules to the polypropylene backbone. A very reactive radical generator is used to create activated bonding sites on the polymer backbone. These radical generators are peroxide molecules that dissociate to form oxygen centered radicals. These radicals then react with the polypropylene and pull off a hydrogen atom leaving a carbon centered radical that can bond with the grafting target molecule. 2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane, also known as Luperox 101, is a widely used radical generator for grafting polypropylene. The grafting procedure can be done in a reactive extruder that heats and mixes the polymer resin, the radical generator and the grafting target.

Hazards

Hazards were only assessed on the radical generation chemical, 2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane or Luperox 101. The summary of the assessment is in Table 6 and further information is in Appendix I. The radical generator is highly reactive and has been shown to be cytotoxic. It is corrosive to skin, but shows no signs of carcinogenicity or mutagenicity and developmental or reproductive toxicity. There is a data gap in our assessment for sensitization, which would be important for someone repeatedly coming in contact with this chemical either in manufacturing or in use.

Feasibility

The process of grafting polypropylene is well established. However, there is no documentation on grafting pigments to the polypropylene backbone. The feasibility of this strategy depends on the survival of the pigment during the grafting procedure. As noted above, the grafting procedure employs a very reactive radical generator, which breaks a bond in the polymer to create an open binding site. It is possible that the radical generator may also attack the pigment. In order to

implement this strategy, research must be done to investigate which, if any, pigments can survive the grafting environment and bind to the polymer backbone.

Another consideration for the implementation of this strategy is the effect grafting has on the mechanical properties of the polymer. The radical generator can also produce polymer strand breakages or initiate polymer strand branching in addition to opening binding sites. These secondary processes may change the overall mechanical properties of the grafted polypropylene. A potential option for mitigating any change in mechanical property would be to graft a portion of polypropylene with a much higher concentration of pigment than is required in the final product. This grafted polypropylene can then be diluted with pure polymer resin in the molding procedure. It is expected that the grafted polypropylene and the pure polypropylene would be miscible and therefore an even color would be achieved.

Maleated Polypropylene

In the scientific literature, there is one chemical that dominates grafting polypropylene research – maleic anhydride. Maleated polypropylene is polypropylene that has been grafted with maleic anhydride and is shown in Fig.4. The maleic anhydride provides an easily activated binding site for a pigment to bind. Whereas the previous strategy binds the pigment directly to the polypropylene backbone, this strategy accomplishes the same goal with the use of an intermediary molecule. Heating maleated polypropylene will cause the maleic anhydride ring to open, which will allow a pigment to bind to either the dangling oxygen or carbon. This procedure can also be done in a reactive extruder similar to the grafting procedure.

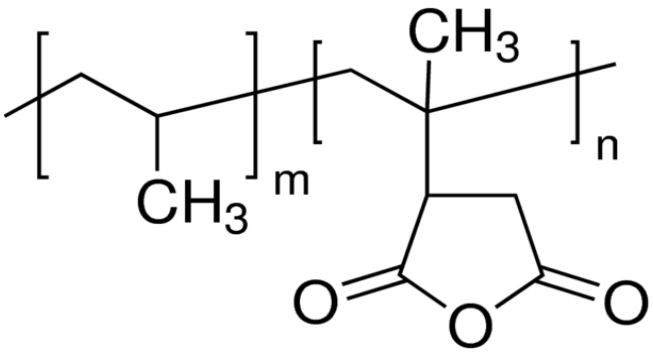

Figure 4. Schematic of maleated polypropylene.

Hazards

Hazards were only assessed on the maleated polypropylene polymer and not the monomers used in its manufacturing. The summary of the assessment is in Table 6 and further information is in Appendix I. Unfortunately, there are data gaps for carcinogenicity or mutagenicity and

reproductive or developmental toxicity. The polymer is also considered a skin sensitizer which may be a concern for people that repeatedly come in contact with the polymer. The polymer is also very persistent, which is similar to other polymers. Otherwise, the polymer is fairly inert with low environmental and acute toxicity.

Table 6. Hazard Assessment for Grafting and Maleated Polypropylene

Less Hazardous → More Hazardous (1 → 4)	Maleated Polypropylene	Luperox 101
Carcinogenicity / Mutagenicity	**No data**	**2**
Reproductive / Developmental Toxicity	**No data**	**1**
Sensitization	**3**	**No Data**
Persistence / Bioaccumulation	**3**	**2**
Environmental Toxicity	**1**	**2**
Acute Toxicity	**1**	**4**

Feasibility

Maleated polypropylene is commercially available and can be substituted for pure polypropylene in the manufacturing process. The feasibility assessment of this strategy is very similar to the grafting strategy. A pigment must be able to bind with the ring opened maleic anhydride for this strategy to work. As an example, any pigment with an OH group can bind to the maleic anhydride. Further research must be done to identify the pigments that can and cannot bind to maleic anhydride.

In regards to the mechanical properties of the polymer, maleated polypropylene has slightly different properties than pure polypropylene. Similar to the grafting case, a highly pigmented

sample can be diluted and dispersed within pure polypropylene to mitigate any changes in the mechanical properties of the final product.

Polypropylene Binding Peptides

Nature has a way of selectively binding target molecules, which is exemplified by cell surface receptors. These protein receptors are embedded in a cell membrane and selectively bind extracellular molecules. Our proposed strategy is a translation of that biological process to achieve our goal of replacing freely flowing additives with compound that are bound to the polymer backbone.

Patented research describes peptides with a binding affinity for polypropylene that can be used to deliver beneficial agents, such as colorants, to polypropylene surfaces. (Cunningham, Lowe, O'Brien, & Wang, 2011). This system consists of: **polypropylene binding peptides (PPBPs)**, **pigment molecules**, and optional **linker** molecules.

The PPBPs are comprised of 7-50 amino acids and are created using synthetic, recombinant, or combinatorial methods. Even though PPBPs can bind a wide range of target molecules, we are specifically interested in ones that target pigment molecules. As shown in Table 7, there are specific PPBPs that interact with certain colorants (carbon black, Sunfast® Magenta or Sunfast® Blue). While the patent authors state that other organic and inorganic pigments can be used, the PPBPs were designed and patented for optimal use with these three colorants (Cunningham, Lowe, O'Brien, & Wang, 2011).

Table 7. Polypropylene binding peptide sequences for three colorants

Pigment	Peptide sequence		
Carbon black	MPPPLMQ	FHENWPS	RTAPTTPLLLSL
Sunfast® Magenta	YPNTALV	VATRIVS	HSLKNSMLTVMA
Sunfast® Blue	RHDLNTWLPPVK	SVSVGMKPSPRP	SVSVGIQPSPRP

Even though the amino acid sequence differs among PPBPs, they all have two specific domains: the polypropylene binding domain and the target binding domain. The polypropylene binding domain is a specific sequence of amino acids in the peptide that links the peptide to the polypropylene surface. The target binding domain is a specific amino acid sequence within the binding peptide that binds the target molecule to the peptide. These two binding domains allow the PPBPs to attach a pigment molecule to the PP backbone shown in Figure 5. PPBPs accomplish the goal of polymer modularity using a similar approach as grafting PP or maleated

PP. The main difference is that the PPBPs use a biological molecule to attach the pigment to the PP backbone.

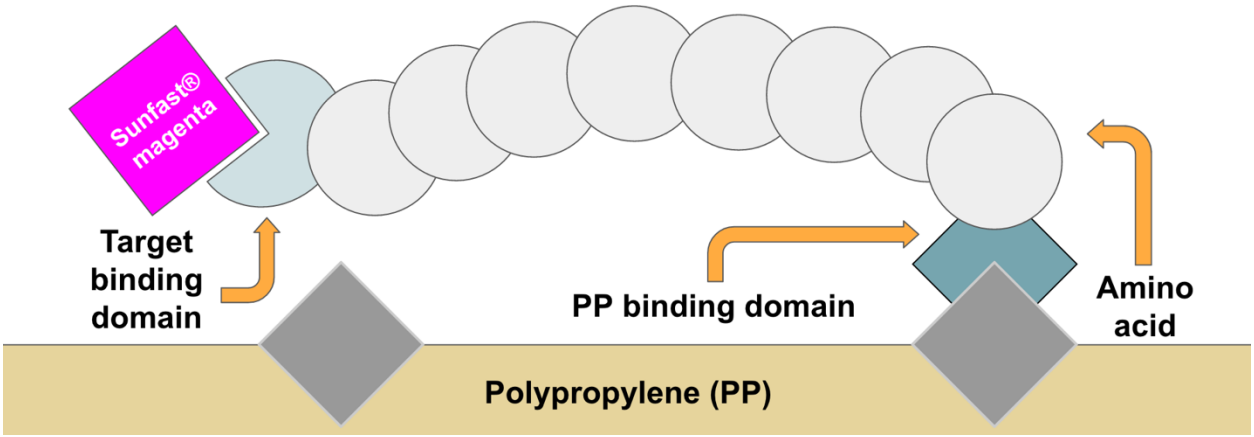

Figure 5. Diagram of PPBP bound to polypropylene and a target molecule

PPBPs can also incorporate linker molecules, which essentially serve the function of a target binding domain while also having another unique ability. Linker molecules are used to either stabilize the bonding of target molecules to the PPBP, or they are designed to break and release the target molecule from the PPBP under certain conditions such as a change in pH or temperature, time, molecular concentration (Cunningham, Lowe, O'Brien, & Wang, 2011). This has interesting implications for both manufacturing and recycling. For example, linker molecules could be used to ensure pigment molecules remain bound to the peptide during harsh (high temperature) manufacturing processes.

Hazards

PPBP Colorants

PPBPs were designed and patented for optimal use with Carbon black, Sunfast® Magenta, and Sunfast® Blue pigments (Cunningham, Lowe, O'Brien, & Wang, 2011). Carbon black is a well-known occupational carcinogen and is suspected of causing reproductive or developmental toxicity and respiratory and skin sensitization (see Table 8). Even though the researchers who patented PPBPs recommended carbon black for use with PPBPs, carbon black presents a significant occupational hazard during manufacturing. If Steelcase is interested in pursuing PPBPs, we would suggest exploring alternative black pigments, such as torrefied walnut shells, that potentially could be bound to PPBPs.

In contrast to carbon black, Sunfast® Blue and Sunfast® Magenta are relatively low hazard pigments. Sunfast® Blue has low hazard ratings in all endpoint categories except persistence and

bioaccumulation due to its chelated copper center. Persistence is inherent in metals, but since the pigment is a low-hazard substance, persistence is of lower concern. Similarly, Sunfast® Magenta has a low hazard profile for four endpoint categories. There is a data gap for reproductive or developmental toxicity, which indicates that more research is needed to fully define the hazard profile for this pigment. However, both of these colorants are promising for use with PPBPs and as potential low hazard alternatives for blue and red-purple pigments.

Table 8. Hazard Assessment for PPBP Colorants

Less Hazardous → More Hazardous (1 → 4)	Carbon Black	Sunfast® Magenta	Sunfast® Blue
Carcinogenicity / Mutagenicity	**4**	**1**	**1**
Reproductive / Developmental Toxicity	**3**	**No data**	**1**
Sensitization	**3**	**No data**	**1**
Persistence / Bioaccumulation	**3**	**1**	**3**
Environmental Toxicity	**1**	**1**	**1**
Acute Toxicity	**4**	**2**	**1**

Linkers

We assessed the hazards for five promising linkers for PPBPs (see Table 9), though there are many additional possible linkers. Four of these linker molecules – ethylene glycol, butylene glycol, ethanol amine, and phenoxy ethanol – have data associated with carcinogenicity and reproductive/developmental toxicity. No such data was available for 1-amino-2-propanol, though this does not mean it is non-hazardous. Additionally, except for ethanol amine, all of these linker molecules have data gaps for sensitization. This endpoint category is of particular concern during the manufacturing process when workers could potentially come into repeated contact with these compounds.

The linker molecules are sensitizers, ecotoxicants, and/or acutely toxic to varying levels and have low persistence and bioaccumulation. Of all the linker molecules, butylene glycol has the most favorable hazard profile especially since it has no known carcinogenicity/mutagenicity and

low acute and aquatic toxicity. We would suggest pursuing this linker molecule if all other performance criteria are equal.

Table 9. Hazard Assessment for PPBP Linkers

Less Hazardous → More Hazardous (1 → 4)	1-amino-2-propanol	Ethylene glycol	Butylene glycol	Ethanol amine	Phenoxy ethanol
Carcinogenicity / Mutagenicity	No data	2	1	2	1
Reproductive / Developmental Toxicity	No data	2	2	2	2
Sensitization	No data	No data	No data	4	No data
Persistence / Bioaccumulation	2	1	1	1	1
Environmental Toxicity	1	2	1	2	2
Acute Toxicity	3	3	1	3	2

Peptides

Finding hazard information for novel oligopeptides is challenging. We searched authoritative lists and primary literature but were unable to find any hazard information for the peptides listed in Table 6. We then searched specialized protein databases (e.g. Protein Data Bank, Protein Basic Local Alignment Search Tool) that are not included in typical hazard aggregation databases. This returned information on larger proteins or peptides that contained similar or homologous peptide sequences to the PPBPs but did not provide meaningful hazard information. Even though there is a lack of specific data on these PPBPs, a well-known concern with peptides in general is their allergenicity. There are many different assays and tests that can help determine the cytotoxic and allergenic activity of peptides (Hartmann, Wal, & Bernard, 2007). Steelcase should investigate the key hazards of cytotoxicity and allergenicity if they want to pursue the PPBP approach.

Feasibility

PPBPs are the longest-term strategy for polymer modularity. Since PPBPs are patented the specific binding mechanism between the peptide and the pigment and peptide and PP is unknown. This information gap makes it difficult to determine why certain pigments are considered optimal for use with PPBPs and if other pigments, such as torrefied walnut shells, could be used as alternatives. It also makes it difficult to determine the technical feasibility of this strategy. Ultimately, this will depend on whether the binding sites can survive the manufacturing conditions for the Node chair.

We envision that the PPBPs could either be applied to the PP pellets before molding the chair seat shell or as a surface modification to the chair seat shell after molding. There are potential complications with both of these applications. One major concern is whether the PPBPs will survive the injection molding process, which is used to form the Node chair. Peptides tend to denature under high heat conditions, and it is unknown if they could maintain their binding functionality under the current molding conditions. One option for this problem is to use a linker molecule. Additionally, it is unclear how the PPBPs would affect the plastic properties of the Node chair while also imparting monodisperse, permanent color.

Applying the PPBPs as a surface modification would not affect the plastic properties of the Node chair seat shell. However, it is unclear if applying PPBPs only to the surfaces of the seat shell will provide long lasting, uniform color. The color fastness of this application would need to be tested under the typical use conditions for the Node chair. If Steelcase is interested in pursuing this strategy, we would first suggest contacting the patent authors to see if they would be willing to share more information about the binding mechanism of these peptides. This would allow feasibility of this strategy and alternative pigments to be more thoroughly assessed.

Polypropylene binding peptides have the potential to provide a way to bind additives to a polymer backbone, which is a necessary step toward the ultimate goal of polymer modularity. This is one potential strategy by which Steelcase can impart color to its Node chair without free-flowing additives. Our initial hazard assessment indicates that despite some concerns, there are a number of promising chemicals that could be used in this strategy, namely the Sunfast® colorants and a butylene glycol linker. We recommend that Steelcase explore less hazardous alternatives because there is still a risk for occupational exposure before the binding occurs. Further research is needed on the toxicity of the PPBPs themselves, as well as how they could be incorporated into Steelcase's current manufacturing process and their potential impact on performance.

Next Steps

Strategy Implementation

The four strategies presented in this work are ordered by ease of implementation from near term to long term solutions. These strategies require changes in the manufacturing procedure, which is outlined in the introduction. Steelcase has the ability to influence change within its manufacturing supply chain, and the following paragraph outlines what these changes may entail.

The torrefied walnut shells are an exchangeable alternative to carbon black and could be supplied by a Tier III colorant supplier. To implement grafting polypropylene, an additional grafting procedure must be introduced between the Tier II polymer supplier and the Tier I injection molding step. Similarly, maleated polypropylene would also require a step between the Tier II polymer supplier and the Tier I injection molding step to bind the pigment to the polymer. Maleated polypropylene would also require a change on the part of the Tier II polymer supplier because a different polymer is required. Implementation of the polypropylene binding peptides is difficult because the exact binding mechanism is unknown. If the peptides can survive the molding procedure, then they can be attached in a step between the Tier II polymer supplier and the Tier I injection molding step. If the peptides are attached after the molding procedure, then an additional step after the Tier I supplier would be needed to coat the seat shell.

Conclusion

Our goal for Steelcase was to impart color to a polymer without the use of hazardous free-flowing additives and envision an approach to polymer modularity that could theoretically enhance the recyclability of plastics. We divided our strategies into two categories to meet Steelcase's needs. Our first strategy addressed the hazards associated with a current colorant, carbon black, by suggesting a less hazardous alternative of torrefied walnut shells. This is a relatively near-term strategy that could be implemented swiftly if Steelcase's Tier 3 suppliers could procure commercial supplies of torrefied walnut shells. It would require minimal alteration to the current manufacturing process. The second strategy category that we explored directly addressed Steelcase's goal of polymer modularity. We identified three promising strategies - grafting polypropylene, maleated polypropylene, and polypropylene binding peptides - that each have varying degrees of technical feasibility. These strategies require alterations to the current manufacturing and recycling processes and thus are longer-term strategies.

Our strategies demonstrate that the chemistry of polymer modularity is possible, though more research is needed on the mechanical properties and technical feasibility of each strategy. Polymer modularity is a long term but promising vision for creating a high quality technical

material for extended use in the circular economy. It will require rethinking both the manufacturing and recycling of plastics. We hope that these strategies and their associated technical and hazard information can help direct Steelcase's future interest and research areas.

Acknowledgements

We would like to acknowledge the many people involved in this project. We would like to thank our instructors – Meg Schwarzman, Tom McKeag, and Akos Kokai – for their guidance, feedback, and expertise in developing this project. We would also like to thank Jon Smieja for initiating this project and for his valuable insight and expertise over the course of this semester. We would also like to acknowledge the many experts, both in polymers and manufacturing, who took the time to talk with us: Clinton Boyd, Megann Head, Steve Wasson, Billy Hart-Cooper, and Lennard Torres.

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Baurhoo, B., Ruiz-Feria, C.A., Zhao, X. Purified lignin: Nutritional and health impacts on animals? A review. *Animal Feed Science and Technology* 144(3): 175-184. 10.1016/j.anifeedsci.2007.10.016

Cunningham, S. D., Lowe, D. J., O'Brien, J. P., & Wang, H. (2011). Polypropylene binding peptides and methods of use. US Patent Office.

Hartmann, R., Wal, J. M., & Bernard, H. (2007). Cytotoxic and allergenic potential of bioactive proteins and peptides. *Current Pharmaceutical …*, *13*(9), 897–920. http://doi.org/10.2174/138161207780414232

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Tulumuru, J.S., Sokhansanj, S., Hess, J.R., Wright, C.T., & Boardman, R.D. (2011). A review on biomass torrefication process and product properties for energy applications. *Industrial Biotechnology* 7(5), 384-402.

Appendix I: Hazard Assessment

Chromium Oxide [1308-38-9]
Cr_2O_3

Carcinogenicity/Mutagenicity: 2

[HSDB] Evaluation: There is inadequate evidence in humans for the carcinogenicity of metallic chromium and of chromium(III) compounds.
IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans. Geneva: World Health Organization, International Agency for Research on Cancer, 1972-PRESENT. (Multivolume work). Available at: http://monographs.iarc.fr/ENG/Classification/index.php , p. V49 213 (1990)

[HSDB] A4; Not classifiable as a human carcinogen. /Chromium and Cr(III) inorganic compounds/
American Conference of Governmental Industrial Hygienists TLVs and BEIs. Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices. Cincinnati, OH 2016, p. 21

The data from oral and inhalation exposures of animals to trivalent chromium do not support documentation of the carcinogenicity of trivalent chromium.
U.S. Environmental Protection Agency's Integrated Risk Information System (IRIS). Summary on Chromium (III), insoluble salts (16065-83-1). Available from, as of October 29, 2015: http://www.epa.gov/iris/

[HSDB] Chronic poisoning: ... Incidence of lung cancer is incr up to 15 times normal in workers exposed to dust of chromite, chromic oxide, & chromium ores.
*Dreisbach, R.H. Handbook of Poisoning. 11th ed. Los Altos, CA: Lange Medical Publications. 1983., p. 251 **PEER REVIEWED***

[HSDB] In experiments with Wistar and random-bred rats (sex, age and distribution unspecified), 4/20 animals developed lung sarcomas 16-19 months after a single intraperitoneal injection of 20 mg chromic oxide.
*IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer, 1972-PRESENT. (Multivolume work). Available at: http://monographs.iarc.fr/index.php, p. V49 120 (1990)] **PEER REVIEWED***

[HSDB] /HUMAN EXPOSURE STUDIES/ In summary, oxidatively damaged urinary guanosine was associated with airborne and systemic exposure to metals in welders and showed a strong relation to body iron stores. /Chromium oxide/[Pesch B et al; Arch Toxicol. 89 (8): 1257-69 (2015)] Full text: PMC4508371 Abstract: PubMed

[HSDB] /ALTERNATIVE and IN VITRO TESTS/ Cr2O3 NPs led to DNA damage, which was deduced by comet assay and cytokinesis block micronucleus assay. Abstract: PubMed

Senapati VA et al; J Appl Toxicol. 35 (10): 1179-88 (2015)
[HSDB] /LABORATORY ANIMALS: Chronic Exposure or Carcinogenicity/ There was no difference in the incidence of pulmonary adenomas between treated mice and 75 untreated controls.
IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans. Geneva: World Health Organization, International Agency for Research on Cancer, 1972-PRESENT. (Multivolume work). Available at: http://monographs.iarc.fr/ENG/Classification/index.php , p. V49 120 (1990)

[HSDB] /LABORATORY ANIMALS: Chronic Exposure or Carcinogenicity/ Rat study: No tumor developed at the injection site.
IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans. Geneva: World Health Organization, International Agency for Research on Cancer, 1972-PRESENT. (Multivolume work). Available at: http://monographs.iarc.fr/ENG/Classification/index.php , p. V49 121 (1990)

[HSDB] /LABORATORY ANIMALS: Chronic Exposure or Carcinogenicity/ in 3 rats given 1%, in 1 given 2% & in 3 given 5%. ... Controls, 1 mammary carcinoma & 2 fibroadenomas were detected.
IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans. Geneva: World Health Organization, International Agency for Research on Cancer, 1972-PRESENT. (Multivolume work). Available at: http://monographs.iarc.fr/ENG/Classification/index.php , p. V23 254 (1980)

[HSDB] /LABORATORY ANIMALS: Chronic Exposure or Carcinogenicity/ No precancerous changes were observed at the implantation sites; one rat, who received a pellet containing welding fumes, showed squamous cell carcinoma remote from the implantation site and not associated with the bronchus. It had the appearance of a metastasis. All three benz(a)pyrene control rats developed cancer at the implantation site. ... Abstract: PubMed
Berg NO et al; Am J Ind Med. 1987;11 (1): 39-54 (1987)

[HSDB] /GENOTOXICITY/ The results indicate the ability of a particulate (Cr(III) compound to induce mutation in a mammalian cell system and the usefulness of such systems for detecting genotoxic insoluble metal compounds. Abstract: PubMed
Elias Z et al; Mutat Res. 169 (3):159-70 (1986)

[HSDB] /ALTERNATIVE and IN VITRO TESTS/ The results suggest toxic effect of very low concentrations of chromium oxide on chromatin and in this reaction both DNA and histones are involved.
Khorsandi K, Rabbani-Chadegani A ; Int J Biol Macromol. 70: 57-63 (2014)

Endocrine disruptor/Reproductive toxicity/Developmental toxicity: 1

[HSDB] /LABORATORY ANIMALS: Developmental or Reproductive Toxicity/ No effects on reproduction were reported in nine pairs of rats fed up to 5% chromium(III) oxide in a supplemented bread, 5 days/week for 60 days ... .
Ivankovic S, Preussman R; Food Cosmet Toxicol 13: 347-51 (1975)

[EPA ACToR] No adverse reproductive effects on pups in rat study
Ivankovic S, Preussman R; Food Cosmet Toxicol 13: 347-51 (1975) as cited in DHHS/ATSDR; Toxicological Profile for Chromium (Draft) p.62

Sensitization: 4

[PHAROS] Respiratory sensitizer - Category 1 [Japan – GHS]

- H334: May cause allergy or asthma symptoms or breathing difficulties if inhaled [Danger Sensitization, respiratory - Category 1]

[PHAROS] Skin sensitizer - Category 1 [Japan – GHS]

- H317: May cause an allergic skin reaction [Warning Sensitization, Skin - Category 1]

[PubChem] Eczematous dermatitis due to trivalent chromium compounds has been reported. /Trivalent chromium compounds/
Lewis, R.J. Sr. (ed) Sax's Dangerous Properties of Industrial Materials. 11th Edition. Wiley-Interscience, Wiley & Sons, Inc. Hoboken, NJ. 2004., p. 919

Persistence/Bioaccumulation: 2

[PHAROS] EC – CEPA DSL – Persistent – Potential Concern
[EPA ACToR] Canada Domestic Substances list – persistent
[EPA ACToR] Canada Domestic Substances list – not bioaccumulative

Aquatic toxicity/Ecotoxicity: 4

[PHAROS] Japan GHS – Acute aquatic - Category 1

- Acute toxicity ≤1.00 mg/l

[PHAROS] Japan GHS – Chronic aquatic - Category 1

- Acute toxicity ≤ 1.00 mg/l and lack of rapid degradability and log Kow ≥ 4 unless BCF < 500

[PHAROS] German FEA – Low hazards to water Class 1
[EPA ACToR] Canada Domestic Substances list – inherently toxic to aquatic organisms

Acute Toxicity: 4

[HSDB] /ALTERNATIVE and IN VITRO TESTS/ The cellular influences of Cr(2)O(3) nanoparticles matched those of hexavalent chromium. In conclusion, Cr(2)O(3) nanoparticles have a high cytotoxic potential. Abstract: PubMed
Horie M et al; Environ Toxicol. 28 (2): 61-75 (2013)

[PubChem] Probably a severe eye, skin, & mucous membrane irritant.
Lewis, R.J. Sr. (ed) Sax's Dangerous Properties of Industrial Materials. 11th Edition. Wiley-Interscience, Wiley & Sons, Inc. Hoboken, NJ. 2004., p. 921

Chronic Toxicity: 4

Organ toxicant - Category 1 [Japan – GHS]

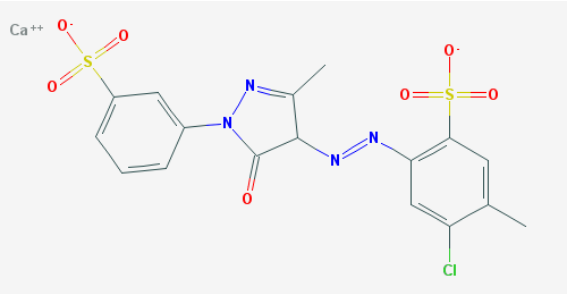
- H372: Causes damage to organs through prolonged or repeated exposure [Danger Specific target organ toxicity, repeated exposure - Category 1]

OTHER

[PubChem] Permissible Exposure Limit: Table Z-1 8-hr Time Weighted Avg: 0.5 mg/cu m. /Chromium(III) compounds, as Cr/
29 CFR 1910.1000 (USDOL); U.S. National Archives and Records Administration's Electronic Code of Federal Regulations. Available from, as of November 3, 2015: http://www.ecfr.gov

[PubChem] Recommended Exposure Limit: 10-hour Time-Weighted Average: 0.5 mg/cu m. /Chromium(III) compounds (as Cr)/
NIOSH. NIOSH Pocket Guide to Chemical Hazards. Department of Health & Human Services, Centers for Disease Control & Prevention. National Institute for Occupational Safety & Health. DHHS (NIOSH) Publication No. 2010-168 (2010). Available from: http://www.cdc.gov/niosh/npg

Pigment Yellow 191 [129423-54-7]



Carcinogenicity/Mutagenicity: 3

[ECHA, Annex III] # Suspected carcinogen: The Toolbox profiler Carcinogenicity (genotox and nongenotox) alerts by ISS gives an alert for carcinogenicity; ISS Carcinogenicity model in VEGA (Q)SAR platform predicts that the chemical is Carcinogen (moderate reliability) #

[ECHA, Annex III] Suspected mutagen: The Toolbox profiler Protein binding alerts for Chromosomal aberration by OASIS v1.1 gives an alert for mutagenicity

Endocrine disruptor/Reproductive toxicity/ Developmental toxicity: Data Gap

Sensitization: 2

[ECHA, Annex III] Suspected skin sensitizer: The Toolbox profiler Protein binding alerts for skin sensitization by OASIS v1.3 gives an alert for skin sensitization

Persistence/Bioaccumulation: 4

[Verdcol MSDS] Non-biodegradable and insoluble in water

Aquatic toxicity/Ecotoxicity: 4

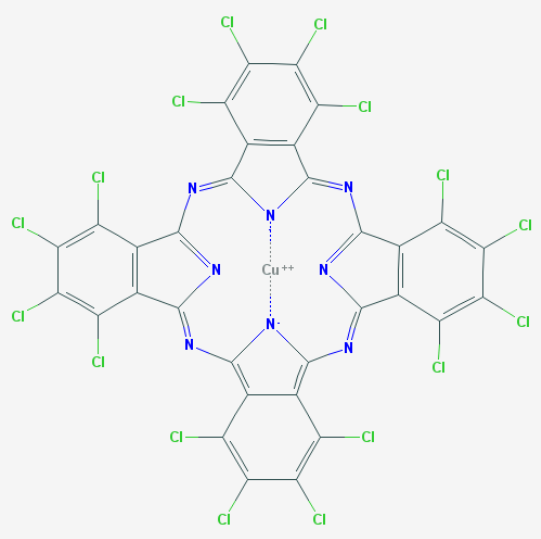
[ECHA] Aquatic Chronic [H412: Harmful to aquatic life with long lasting effects.]

Acute Toxicity: 2

Low oral toxicity in rats [Worksafe Australia]
https://www.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=1&cad=rja&uact=8&ved=0ahUKEwjbga-79eTPAhUowFQKHYrcAXAQFggIMAA&url=https%3A%2F%2Fwww.nicnas.gov.au%2F__data%2Fassets%2Fword_doc%2F0016%2F20374%2FNA519FR.docx&usg=AFQjCNEX5il2znppxMktpheK5wMOvsd6yg

Slight eye and skin irritant in rabbits [Worksafe Australia]
Low dermal toxicity in rats [Worksafe Australia]
https://www.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=1&cad=rja&uact=8&ved=0ahUKEwjbga-79eTPAhUowFQKHYrcAXAQFggIMAA&url=https%3A%2F%2Fwww.nicnas.gov.au%2F__data%2Fassets%2Fword_doc%2F0016%2F20374%2FNA519FR.docx&usg=AFQjCNEX5il2znppxMktpheK5wMOvsd6yg

Phthalocyanine Green [1328-53-6]



Carcinogenicity/Mutagenicity: 1

[EPA ACToR] NLM TOXNET CCRIS Data MSTU - MUTAGENICITY STUDIES
[zeiger,e, anderson,b, haworth,s, lawlor,t and mortelmans,k; salmonella mutagenicity tests: iv. Results from the testing of 300 chemicals; environ. Mol. Mutagen. 11(suppl.12):1-158, 1988]

Dose Range 100-10000 ug/plate (test material solvent: dmso)
Results NEGATIVE

Metabolic activation hamster, liver, s-9, aroclor 1254 (30%)
Results NEGATIVE

Dose range 100-10000 ug/plate (test material solvent: dmso)
Metabolic activation rat, liver, s-9, aroclor 1254 (30%)
Results NEGATIVE

Dose range 100-10000 ug/plate (test material solvent: dmso)
Metabolic activation none
Results NEGATIVE

Dose range 100-10000 ug/plate (test material solvent: dmso)
Metabolic activation hamster, liver, s-9, aroclor 1254 (30%)
Results POSITIVE

Dose range 333-10000 ug/plate (test material solvent: dmso)
Metabolic activation rat, liver, s-9, aroclor 1254 (30%)
Results POSITIVE

Endocrine disruptor/Reproductive toxicity/ Developmental toxicity: Data Gap

Sensitization: Data Gap

Persistence/Bioaccumulation: 3

Persistent – Potential Concern [EC – CEPA DSL]

[EPA ACToR] Not Bioaccumulative – Canada Domestic Substance List
[EPA ACToR] Persistent – Canada Domestic Substance List

Aquatic toxicity/Ecotoxicity: 1

[PHAROS] Low hazards to water – German FEA, Class 1

Acute Toxicity: 2

[ECHA] H312: Harmful in contact with skin.
[ECHA] H319: Causes serious eye irritation.
[ECHA] H335: May cause respiratory irritation.

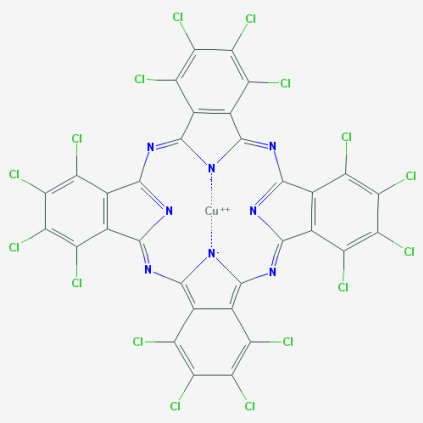
[EPA ACToR] Reported Dose > 10gm/kg (10000mg/kg) [rat] [NLM TOXNET Toxicology]
Khigiena i Zdraveopazvane. Hygiene and Sanitation. Vol. 16, Pg. 191, 1973.

OTHER

[PHAROS] Verified Low Concern [US EPA - DfE SCIL - Green Circle]

[EPA ACToR] Human Health Priorities – Moderate [Canada Domestic Substance List (2007)]

Pigment Red 254 [84632-65-5]



Carcinogenicity/Mutagenicity: 3

[ECHA, Annex III] # Suspected carcinogen: The Toolbox profiler Carcinogenicity (genotox and nongenotox) alerts by ISS gives an alert for carcinogenicity

[ECHA, Annex III] # Suspected mutagen: CAESAR Mutagenicity model in VEGA (Q)SAR platform predicts that the chemical is Mutagen (moderate reliability); KNN Mutagenicity model in VEGA (Q)SAR platform predicts that the chemical is Mutagen (moderate reliability); SARPY Mutagenicity model in VEGA (Q)SAR platform predicts that the chemical is Mutagen (moderate reliability)

ED/Reproductive toxicity/ Developmental toxicity: Data Gap

Sensitization: 2

[PubChem] Minor or no respiratory hazard – very minor effects in lung tissue in rat study *Hoffman et al. (http://www.tandfonline.com/doi/full/10.1080/08958378.2016.1200698)*

[ECHA, Annex III] # Suspected skin sensitizer: The Toolbox profiler Protein binding alerts for skin sensitization by OASIS v1.3 gives an alert for skin sensitization

Persistence/Bioaccumulation: 1

[EPA ACToR] Canada Domestic Substances list – not bioaccumulative
[EPA ACToR] Canada Domestic Substances list – not persistent

Aquatic toxicity/ecotoxicity: 2

[PHAROS] German FEA – Low hazards to water - Class 1
[EPA ACToR] Canada Domestic Substances list – inherently toxic to aquatic organisms

Acute Toxicity: Data Gap

Titanium Dioxide [13463-67-7]
TiO_2

Carcinogenicity/Mutagenicity: 4

[PHAROS] US CDC Occupational carcinogen – high hazard level

[PubChem] GHS H351: Suspected of causing cancer [Warning Carcinogenicity - Category 2]

[HSDB, OSHA] Cancer in humans: There is inadequate evidence in humans for the carcinogenicity of titanium dioxide. Cancer in experimental animals: There is sufficient evidence in experimental animals for the carcinogenicity of titanium dioxide. Overall evaluation: Titanium dioxide is possibly carcinogenic to humans (Group 2B).
IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans. Geneva: World Health Organization, International Agency for Research on Cancer, 1972-PRESENT. (Multivolume work). Available at: http://monographs.iarc.fr/ENG/Classification/index.php , p. V93 275 (2010)

[HSDB, OSHA] A4: Not classifiable as a human carcinogen.
American Conference of Governmental Industrial Hygienists TLVs and BEIs. Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices. Cincinnati, OH 2010, p. 57

[HSDB, OSHA] 5000 mg/cu m; NIOSH considers titanium dioxide to be a potential occupational carcinogen.
NIOSH. NIOSH Pocket Guide to Chemical Hazards & Other Databases CD-ROM. Department of Health & Human Services, Centers for Disease Prevention & Control. National Institute for Occupational Safety & Health. DHHS (NIOSH) Publication No. 2005-151 (2005)

[HSDB, OSHA] NIOSH considers titanium dioxide to be a potential occupational carcinogen.
NIOSH. NIOSH Pocket Guide to Chemical Hazards. Department of Health & Human Services, Centers for Disease Control & Prevention. National Institute for Occupational Safety & Health. DHHS (NIOSH) Publication No. 2010-168 (2010). Available from: http://www.cdc.gov/niosh/npg

[HSDB] NIOSH usually recommends that occupational exposures to carcinogens be limited to the lowest feasible concentration.
NIOSH. NIOSH Pocket Guide to Chemical Hazards. Department of Health & Human Services, Centers for Disease Control & Prevention. National Institute for Occupational Safety & Health. DHHS (NIOSH) Publication No. 2010-168 (2010). Available from: http://www.cdc.gov/niosh/npg

[HSDB] /EPIDEMIOLOGY STUDIES/ The results of the study do not suggest a carcinogenic effect of TiO2 dust on the human lung.
*Boffetta P et al; Cancer Causes Control 15 (7): 697-706 (2004) **PEER REVIEWED** PubMed Abstract*

[HSDB] /GENOTOXICITY/ Photo-illumination of TiO2 (anatase/rutile samples of various ratios; particle size not known) catalyzed oxidative DNA damage in cultured human fibroblast cells, which the assay indicated was due to hydroxyl radicals.
*NIOSH/CDC; Current Intelligence Bulletin 63: Occupational Exposure to Titanium Dioxide p23 (April 2011). Available from, as of October 31, 2013: http://www.cdc.gov/niosh/pubs/cib_date_desc_nopubnumbers.html **PEER REVIEWED***

[HSDB] /GENOTOXICITY/ In total darkness, a slightly higher level of oxidative DNA damage was also detected with treatment using an anatase-rutile mixture than with treatment using either the anatase or rutile forms alone. These results suggest that intratracheal instillation of ultrafine TiO(2) particles may cause an inflammatory response.
*Gurr JR et al; Toxicology 213 (1-2): 66-73 (2005) **PEER REVIEWED** PubMed Abstract*

[HSDB] /EPIDEMIOLOGY STUDIES/ Although titanium dioxide (TiO2) is generally regarded as a nontoxic mild pulmonary irritant, some laboratory studies have reported lung adenomas in rats exposed to high levels of TiO2… Results from our study indicate that the exposures at these United States plants are not associated with increases in the risk of death from cancer or other diseases. Moreover, workers with likely higher levels of TiO2 exposure had similar mortality patterns to those with less exposure, as internal analyses among workers revealed no increase in mortality by level of TiO2 exposure.
*[Fryzek JP et al; J Occup Environ Med 45 (4): 400-9 (2003)] **PEER REVIEWED** PubMed Abstract*

[HSDB] /EPIDEMIOLOGY STUDIES/ Cohort analyses suggest that the risks of developing lung cancer and other fatal respiratory diseases were no higher for titanium dioxideexposed employees than for the referent groups.
*[Chen JL, Fayerweather WE; J Occup Med 30 (12): 937-42 (1988)] **PEER REVIEWED** PubMed Abstract*

ED/Reproductive toxicity/ Developmental toxicity: Data Gap

Sensitization: 3

[OSHA] Nuisance particulate – Accumulation in lungs (HE19)

[HSDB] /EPIDEMIOLOGY STUDIES/ A study of 67 subjects in a small titanium oxide paint factory in Nigeria showed 50-54% frequency for airway symptoms, 20-40% for neurological symptoms, and 10-27% for other symptoms. … These findings indicate the need for worker protection in a manufacturing plant in Nigeria.
*[Oleru UG; Am J Ind Med 12 (2): 173-80 (1987)] **PEER REVIEWED** PubMed Abstract*

[HSDB] /ALTERNATIVE and IN VITRO TESTS/ Rats exposed to high airborne mass concentrations of low-solubility low-toxicity particles (LSLTP) have been reported to develop lung disease such as fibrosis and lung cancer... Both sets of data suggested a threshold in dose

measured as surface area of particles relative to the surface area of the exposed cells, at around 1-10 sq cm/sq cm.
*[Monteiller C et al; Occup Environ Med 64 (9): 609-15 (2007)] **PEER REVIEWED** PubMed Abstract Full text: PMC2092561*

Persistence/Bioaccumulation: 2

[PHAROS] European Commission CEPA DSL – potential persistence concerns

Aquatic toxicity/ecotoxicity: 2

[PHAROS] Japan GHS – chronic aquatic toxicant (medium hazard)
[PHAROS] German FEA – non-hazardous to waters (very low hazard)

Acute Toxicity: 3

[PHAROS] Japan GHS – organ toxicant, Category 1 (high hazard)
[PHAROS] Quebec DSST – acute mammalian toxicant (medium hazard)
[PHAROS, PubChem] Japan GHS – eye irritant (medium hazard)

Chronic Toxicity: 1

[HSDB] /OTHER TOXICITY INFORMATION/ Ingested titanium dioxide is considered practically nontoxic. One pound has been ingested without harm and was eliminated in feces within 24 hours.
*[American Conference of Governmental Industrial Hygienists. Documentation of the TLV's and BEI's 7th Edition. Warfarin p.1 CD-ROM Cincinnati, OH 45240-4148 2013.] **PEER REVIEWED***

OTHER

[HSDB] Permissible Exposure Limit: Table Z-1 8-hr Time Weighted Avg: 15 mg/cu m. /Total dust/
29 CFR 1910.1000 (USDOL); U.S. National Archives and Records Administration's Electronic Code of Federal Regulations. Available from, as of October 18, 2013: http://www.ecfr.gov/cgi-bin/ECFR?page=browse

[HSDB] /ALTERNATIVE and IN VITRO TESTS/ Using ESR, we found that most pigments from photocytotoxic inks generated hydroxyl radicals when photoexcited with UV radiation. Therefore, the possibility of photocytotoxicity should be considered when evaluating the safety of permanent makeup inks containing TiO2.
*[Wamer WG, Yin JJ; J Cosmet Sci 62 (6): 535-47 (2011)] **PEER REVIEWED** PubMed Abstract*

Carbon black [1333-86-4]

Carcinogenicity/Mutagenicity: 4

[PHAROS] Occupational carcinogen – high hazard level (US CDC)
[PHAROS, HSDB] Possibly carcinogenic to humans - inhaled from occupational sources [IARC - Group 2B]
[PHAROS] Evidence of carcinogenic effects but not sufficient for classification [MAK - Carcinogen Group 3B]
[PHAROS] Suspected human carcinogens [New Zealand - GHS - 6.7B]
[PHAROS] Carcinogenicity [Japan - GHS - Category 2]
[PHAROS] Carcinogen - specific to chemical form or exposure route [CA EPA - Prop 65]

[HSDB] Many animal laboratory studies confirming carcinogenicity

[HSDB] A4; Not classifiable as a human carcinogen.
*[American Conference of Governmental Industrial Hygienists TLVs and BEIs. Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices. Cincinnati, OH, 2008, p. 17] **PEER REVIEWED***

Endocrine disruptor/Reproductive toxicity/ Developmental toxicity: 3

EPIDEMIOLOGY STUDIES/ … The workers involved in packaging carbon black had increased morbidity from heart disease, influenza, mucous membrane inflammation, and oral and skin diseases; women also had an increased incidence of unidentified diseases of the reproductive organs. Workers who packaged lamp and furnace blacks had higher morbidity than those packaging active or semiactive carbon blacks; they also suffered from acute gastrointestinal diseases and bronchitis.
*[Komarova LT; Nauchn Tr Omsk Med Inst 61: 115-21 (1965) as cited in NIOSH; Criteria Document: Carbon Black p.15 (1978) DHEW Pub. NIOSH 78-204] **PEER REVIEWED** [HSDB]*

Sensitization: 3

[HSDB] Respiratory syncytial virus (RSV) is the major cause of bronchiolitis and pneumonia in infants and may lead to the development of asthma in childhood. … These data indicate that preexposure to ultrafine particles induces an inflammatory milieu promoting allergic immune responses rather than IFNgamma production necessary for microbial defense.
*[Lambert AL et al; Toxicol Sci 72 (2): 331-8 (2003)] **PEER REVIEWED** PubMed Abstract*

[HSDB] HUMAN EXPOSURE STUDIES/ Non-cancer respiratory effects in carbon black workers that have been reported include cough, sputum production, bronchitis, chest radiographic opacities (eg, pneumoconiosis) and decrements in lung function.
*[IARC; Carbon Black (Group 2B)/Prepublication copy from Monograph 93 posted February 27, 2006. Available athttp://monographs.iarc.fr/ENG/Meetings/93-carbonblack.pdf on March 10, 2009] **PEER REVIEWED***

[HSDB] SIGNS AND SYMPTOMS/ Long-term (chronic): Inhalation of carbon black can cause cough, phlegm, tiredness, chest pain, and headache. Dermal, mucosal, or inhalation exposure can cause irritation.
*[Mackison, F. W., R. S. Stricoff, and L. J. Partridge, Jr. (eds.). NIOSH/OSHA - Occupational Health Guidelines for Chemical Hazards. DHHS(NIOSH) Publication No. 81-123 (3 VOLS). Washington, DC: U.S. Government Printing Office, Jan. 1981.] **PEER REVIEWED***

[HSDB] SIGNS AND SYMPTOMS/ ... Most reports describe the effect of carbon black on the lung of human's certain changes which are typical for pneumoconiosis and changes that are suspected to become pneumoconiosis in the future. There were many studies describing carbon black pneumoconiosis from 1951 to 1994. This disease, therefore, has been considered as an occupational disease of workers exposed to carbon black in its production and usage.
*[Szozda R; J UOEH 18 (3): 223-8 (1996)] **PEER REVIEWED** PubMed Abstract [HSDB]*

Persistence/Bioaccumulation: 3

[PHAROS] Persistent [EC – CEPA DSL]

Aquatic toxicity/ecotoxicity: 1

[PHAROS] Very low hazards to water [German FEA - Class 0]

Acute Toxicity: 4

[PHAROS] Acute mammalian toxicant – Medium [Quebec CSST Class D2A]

[PHAROS] Organ toxicant - Category 1 [Japan – GHS] (substances that have produced significant toxicity in humans, or that, on the basis of evidence from studies in experimental animals can be presumed to have the potential to produce significant toxicity in humans following single exposure)

[HSDB] EPIDEMIOLOGY STUDIES/ … Workers who packaged lamp and furnace blacks had higher morbidity than those packaging active or semiactive carbon blacks; they also suffered from acute gastrointestinal diseases and bronchitis.
*[Komarova LT; Nauchn Tr Omsk Med Inst 61: 115-21 (1965) as cited in NIOSH; Criteria Document: Carbon Black p.15 (1978) DHEW Pub. NIOSH 78-204] **PEER REVIEWED***

[HSDB] LD50 Rat oral /greater than/ 8000 mg/kg bw.
*[European Commission, ESIS; IUCLID Dataset, Carbon Black (1333-86-4) p 71 (2000 CD-ROM edition). Available from, as of March, 10 2009: http://esis.jrc.ec.europa.eu/ **PEER REVIEWED***

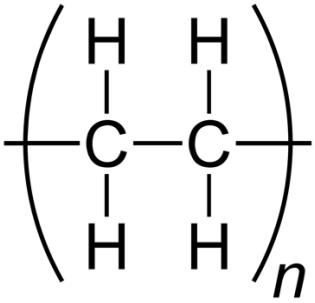
[ToxNet] Somnolence in rats – > 15400mg/kg (15400mg/kg)
Acute Toxicity Data. Journal of the American College of Toxicology, Part B. Vol. 15

[PHAROS] Eye irritation – High [New Zealand GHS]
[PHAROS] Skin irritation – Medium [New Zealand GHS]

[HSDB] May cause skin and respiratory irritation.
*[NIOSH; Criteria Document: Carbon Black p.3 (1978) DHEW Pub. NIOSH 78-204] **PEER REVIEWED***

[HSDB] As superficial foreign bodies, carbon black ... may be slightly irritating mechanically and may cause discoloration of lids and conjunctivae, but they are chemically inert.
*[Grant, W.M. Toxicology of the Eye. 3rd ed. Springfield, IL: Charles C. Thomas Publisher, 1986., p. 178] **PEER REVIEWED***

Polyethylene [9002-88-4]



Carcinogenicity/Mutagenicity: 1

[HSDB] Evaluation: There is inadequate evidence in humans for the carcinogenicity of ethylene. There is inadequate evidence in experimental animals for the carcinogenicity of ethylene. Overall evaluation: Ethylene is not classifiable as to its carcinogenicity to humans (Group 3). (pubchem, *IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans. Geneva: World Health Organization, International Agency for Research on Cancer, 1972-PRESENT. (Multivolume work). Available at: http://monographs.iarc.fr/ENG/Classification/index.php , p. 60 64 (1994)*

[HSDB] A4; Not classifiable as a human carcinogen.
American Conference of Governmental Industrial Hygienists TLVs and BEIs. Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices. Cincinnati, OH, 2008, p. 29

Endocrine disruptor/Reproductive toxicity/ Developmental toxicity: Data Gap

Sensitization: 3

[PHAROS] Quebec CSST - Asthma Agents - Agent Causing Occupational Asthma (respiratory sensitizer, medium hazard)

Persistence/bioaccumulation: 2

[PHAROS] European Commission CEPA DSL – potential persistence concerns

Aquatic toxicity/ecotoxicity: 3

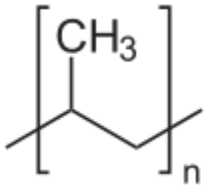
[PHAROS] H402: Harmful to aquatic life [Hazardous to the aquatic environment, acute hazard - Category 3]

[PHAROS] H412: Harmful to aquatic life with long lasting effects [Hazardous to the aquatic environment, long-term hazard - Category 3]

Acute Toxicity: 2

[PHAROS] GHS: Specific target organ toxicity, single exposure; Narcotic effects - Category 3

Polypropylene [9003-07-0]



Carcinogenicity/Mutagenicity: 1

[HSDB] IARC - Group 3 - Agent is not classifiable as to its carcinogenicity to humans
Inadequate evidence of carcinogenicity in animals. OVERALL EVALUATION: Group 3: The agent is not classifiable as to its carcinogenicity to humans.[IARC. Monographs on the *Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer, 1972-PRESENT. (Multivolume work). Available at: http://monographs.iarc.fr/index.php, p. S7 70 (1987)] **QC REVIEWED***

Endocrine disruptor/Reproductive toxicity/ Developmental toxicity: Data Gap

Sensitization: 3

[CHE - Toxicant Database] - Asthma - allergen, sensitizer - strong evidence
[Hazmap] Asthmagen; CHE: Asthma - Allergic Strong; NJDOH: Known Sensitizer

Persistence/Bioaccumulation: 2

[PHAROS] European Commission CEPA DSL – potential persistence concerns
[EPA ACToR] Canada Domestic Substances list – not bioaccumulative
[EPA ACToR] Canada Domestic Substances list – persistent

Aquatic toxicity/Ecotoxicity: 1

[PHAROS] Canada Domestic Substances list – not inherently toxic to aquatic organisms

Acute Toxicity: 2

Organ Toxicity [Japan GHS – Specific target organs / systemic toxicity following single exposure (Cat.3)]

- May cause respiratory irritation
- May cause drowsiness or dizziness

OTHER

[PHAROS] EPA Green Circle – Verified Low Concern

Lignin [9005-53-2]

Carcinogenicity/Mutagenicity: Data Gap

Endocrine disruptor/Reproductive toxicity/ Developmental toxicity: Data Gap

Sensitization: Data Gap

Persistence/Bioaccumulation: 1

Can be broken down by organisms in the environment, typically excreted by humans in the digestive tract (too large to be absorbed through other channels)

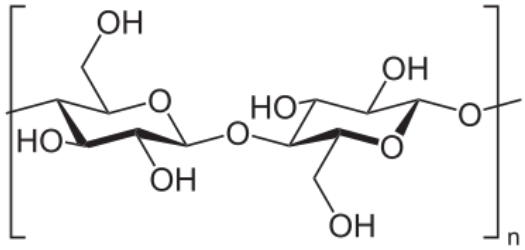
Aquatic toxicity/ecotoxicity: 1

[EPA ACToR] Not inherently toxic to aquatic organisms, Canada Domestic Substances List

Acute Toxicity: 2

Some changes to organ systems in mice after oral administration (https://www.ncbi.nlm.nih.gov/pubmed/10218131)

Cellulose [9004-34-6]



Carcinogenicity/Mutagenicity: 1

[EPA ACToR] No carcinogenic effect in rat study
Wood dust – high carcinogen hazard under CA EPA – depends on physical form

Endocrine disruptor/Reproductive toxicity/ Developmental toxicity: Data Gap

Sensitization: Data Gap

Persistence/Bioaccumulation: 1

Can be broken down by organisms in the environment, typically excreted by humans in the digestive tract (too large to be absorbed through other channels)

Aquatic toxicity/ecotoxicity: 1

[EPA ACToR] Not inherently toxic to aquatic organisms, Canada Domestic Substances List

Acute Toxicity: 2

Health effect: Gastrointestinal and liver	Suspected of or causing an adverse health effect

[PubCHem] H335 (44.44%): May cause respiratory irritation [Warning Specific target organ toxicity, single exposure; Respiratory tract irritation - Category 3]

Health effect: respiratory	Suspected of or causing an adverse health effect
Health effect: Skin. eye, sensory organ	Suspected of or causing an adverse health effect

OTHER

[EPA ACToR] EU Reach – exempted from listing due to intrinsic safety
[EPA ACToR] EPA Green Circle Verified Low Concern

Hemicellulose [9034-32-6]

Carcinogenicity/Mutagenicity: Data Gap

Endocrine disruptor/Reproductive toxicity/ Developmental toxicity: Data Gap

Sensitization: Data Gap

Persistence/Bioaccumulation: Data Gap

Can be broken down by organisms in the environment, typically excreted by humans in the digestive tract (too large to be absorbed through other channels)

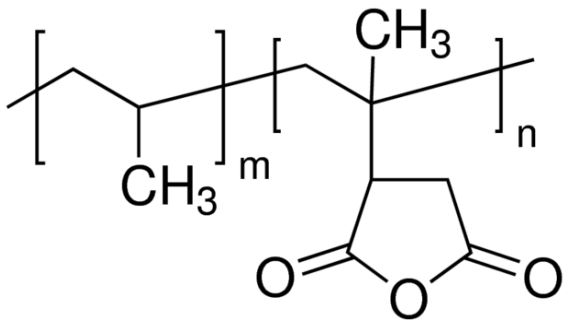
Aquatic Toxicity/Ecotoxcity: Data Gap

Acute Toxicity: Data Gap

OTHER

[EPA ACToR] EPA Green Circle Verified Low Concern

Maleated Polypropylene [25722-45-6]



Carcinogenicity/Mutagenicity: Data Gap

Endocrine disruptor/Reproductive toxicity/ Developmental toxicity: Data Gap

Sensitization: 3

[MSDS] Inhalation: At elevated temperatures, vapor may cause allergic respiratory reaction. *(http://ws.eastman.com/ProductCatalogApps/PageControllers/MSDS_PC.aspx?Product=71015384)*

Persistence/Bioaccumulation: 3

[PHAROS] European Commission CEPA DSL – potential persistence concerns

Aquatic Toxicity/Ecotoxicity: 1

[MSDS] Specified substance(s): maleated polypropylene LC-50 (Fathead Minnow, 96 h): > 100 mg/l (highest concentration tested) maleic anhydride LC-50 (Bluegill Sunfish, 96 h): 75 mg/l

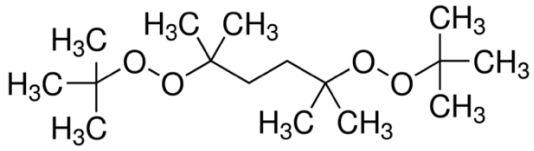
Acute Toxicity: 1

[MSDS] Ingestion: None known effects

OTHER

[PHAROS] EPA Green Circle

Luperox 101, 2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane [78-63-7]



Carcinogenicity/Mutagenicity: 2

[PubChem] Active - qHTS assay for identifying genotoxic compounds that show differential cytotoxicity against isogenic chicken DT40 cell lines with known DNA damage response pathways - Rev3 mutant cell line
[PubChem] Inacitve - qHTS assay for identifying genotoxic compounds that show differential cytotoxicity against a panel of isogenic chicken DT40 cell lines with known DNA damage response pathways

Endocrine disruptor/Reproductive toxicity/ Developmental toxicity: 1

[PubChem] Inclonclusice - qHTS assay for small molecule antagonists of thyroid hormone receptor beta signaling
[PubChem] Inconclusive - qHTS assay for small molecule antagonists of estrogen receptor alpha signaling
[PubChem] Inactive - qHTS assay for small molecule agonists of estrogen receptor alpha signaling
[PubChem] Inactive - qHTS assay for small molecules that induce genotoxicity in human embryonic kidney cells expressing luciferase-tagged ATAD5

Sensitization: Data Gap

Persistence/Bioaccumulation: 2

[PHAROS] CEPA – Bioaccumulative
[PubChem] Insoluble in water
[PHAROS] CEPA - Persistent

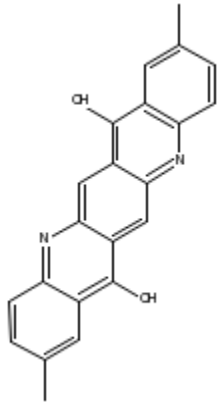
Aquatic Toxicity/Ecotoxicity: 1

[PHAROS] German FEA – Low Hazard to Waters Class 1
[PHAROS] CEPA – Inherently Toxic in the Environment

Acute Toxicity: 4

[PubChem] H315: Causes skin irritation [Skin corrosion/irritation - Category 2]
[PubChem] H319: Causes serious eye irritation [Serious eye damage/eye irritation - Category 2A]
[PubChem] Ingestion or contact (skin, eyes) with substance may cause severe injury or burns.

Sunfast ® Magenta 122 [980-26-7/16043-40-6]



Carcinogenicity/ Mutagenicity: 1

[EPA ACToR] Not genotoxic, based on a bacterial reverse mutation assay

Endocrine disruptor/Reproductive toxicity/ Developmental toxicity: Data Gap

Sensitization: Data Gap

Persistence/Bioaccumulation: 1

[EPA ACToR] Canada Domestic Substance List – not bioaccumulative or persistent

Aquatic toxicity/ecotoxicity: 1

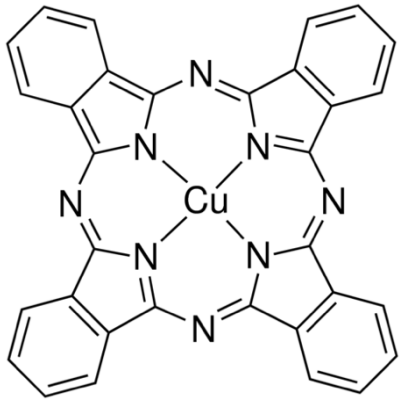
[PHAROS] German FEA Class 1 – Low Hazard to Waters

Acute Toxicity: 2

[EPA ACToR] Not irritating, based on a rabbit study

[PubChem] Gastrointestinal hypermotility and diarrhea from a rat study at 23 g/kg (PubChem)
Acute Toxicity Data. Journal of the American College of Toxicology, Part B. Vol. 15

Sunfast ® Blue 15:3 [147-14-8]



Carcinogenicity/ Mutagenicity: 1

[HSDB] LABORATORY ANIMALS: Chronic Exposure or Carcinogenicity/ Carcinogenicity /study in mice (strain not identified)/, 0.5 mg sc per animal, 34 times/week for 8 months. 17/20 survived /until end of study/. No tumors were found.
*[European Commission, ESIS; IUCLID Dataset, Tetrabenzo-5,10,15,20-diazaporphyrinephthalocyanine (147-14-8) p.35 (2000 CD-ROM edition). Available from, as of April 27, 2010: http://esis.jrc.ec.europa.eu/ **PEER REVIEWED***

[HSDB] GENOTOXICITY/ Preincubation assay with and without metabolic activation, Salmonella typhimurium, strains: TA98, TA100, TA102, TA97. All variants of the test were negative for mutagenicity, both with and without metabolic activation.
*[Organization for Economic Cooperation and Development; Screening Information Data Set for Copper phthalocyanine, CAS #147-14-8 p.139 (1993). Available from, as of April 27, 2010: http://www.chem.unep.ch/irptc/sids/OECDSIDS/sidspub.html **PEER REVIEWED***

[HSDB] GENOTOXICITY/ Preincubation assay and spot test with and without metabolic activation, Salmonella typhimurium, strains: TA1538, TA1535. Negative results, with and without metabolic activation.
*[Organization for Economic Cooperation and Development; Screening Information Data Set for Copper phthalocyanine, CAS #147-14-8 p.139-40 (1993). Available from, as of April 27, 2010: http://www.chem.unep.ch/irptc/sids/OECDSIDS/sidspub.html **PEER REVIEWED***

[HSDB] GENOTOXICITY/ Suspension assay with and without metabolic activation, Salmonella typhimurium, strains: TA98, TA100. Negative for mutagenicity, with and without activation.
*[Organization for Economic Cooperation and Development; Screening Information Data Set for Copper phthalocyanine, CAS #147-14-8 p.140 (1993). Available from, as of April 27, 2010: http://www.chem.unep.ch/irptc/sids/OECDSIDS/sidspub.html **PEER REVIEWED***

[HSDB] GENOTOXICITY/ [Hamster study] The test substance was negative for the mutagenic effect under the test conditions used. (No chromosomal aberrations were observed). The lowest concentration producing cell toxicity: with metabolic activation > 2.0mg/mL, without metabolic

activation = 1.3mg/mL.
*[Organization for Economic Cooperation and Development; Screening Information Data Set for Copper phthalocyanine, CAS #147-14-8 p.141 (1993). Available from, as of April 27, 2010: http://www.chem.unep.ch/irptc/sids/OECDSIDS/sidspub.html **PEER REVIEWED***

[HSDB] GENOTOXICITY/ Mammalian cell gene mutation assay, mouse lymphoma L5178Y TK +/-. Result: negative.
*[European Commission, ESIS; IUCLID Dataset, Tetrabenzo-5,10,15,20-diazaporphyrinephthalocyanine (147-14-8) p.33 (2000 CD-ROM edition). Available from, as of April 27, 2010: http://esis.jrc.ec.europa.eu/ **PEER REVIEWED***

[HSDB] GENOTOXICITY/ Unscheduled DNA synthesis, rat hepatocytes. Result: negative.
*[European Commission, ESIS; IUCLID Dataset, Tetrabenzo-5,10,15,20-diazaporphyrinephthalocyanine (147-14-8) p.34 (2000 CD-ROM edition). Available from, as of April 27, 2010: http://esis.jrc.ec.europa.eu/ **PEER REVIEWED***

GENOTOXICITY/ Cell transformation assay, C3H/1oT1/2 CL8 cells. Result: negative.
*[European Commission, ESIS; IUCLID Dataset, Tetrabenzo-5,10,15,20-diazaporphyrinephthalocyanine (147-14-8) p.35 (2000 CD-ROM edition). Available from, as of April 27, 2010: http://esis.jrc.ec.europa.eu/ **PEER REVIEWED** [HSDB]*

[SDS] Hamster – fibroblast negative
[SDS] Ames test on S. typhimurium; negative
[SDS] Mouse – mutation in mammalian somatic cells; negative

Endocrine disruptor/Reproductive toxicity/ Developmental toxicity: 1

[HSDB] LABORATORY ANIMALS: Developmental or Reproductive Toxicity/ [rat study] The substance was negative for reproductive toxicity observed in parental animals (fertility, gestation, reproductive organ toxicity etc.).
*[Organization for Economic Cooperation and Development; Screening Information Data Set for Copper phthalocyanine, CAS #147-14-8 p.143 (1993). Available from, as of April 27, 2010: http://www.chem.unep.ch/irptc/sids/OECDSIDS/sidspub.html **PEER REVIEWED** [HSDB]*

[HSDB] LABORATORY ANIMALS: Developmental or Reproductive Toxicity/ [Rat study] No teratogenic effects observed under the test conditions used.
*[Organization for Economic Cooperation and Development; Screening Information Data Set for Copper phthalocyanine, CAS #147-14-8 p.145 (1993). Available from, as of April 27, 2010: http://www.chem.unep.ch/irptc/sids/OECDSIDS/sidspub.html **PEER REVIEWED** [HSDB]*

Sensitization: 1

[SDS] Guinea Pig – does not cause skin sensitization

[HSDB] LABORATORY ANIMALS: Acute Exposure/ Phthalocyanine blue was apparently non-irritating to the skin and eye of rabbits. It evidently gave no evidence of sensitization in an animal study.
*[The British Industrial Biological Research Association; Toxicity Profile: Phthalocyanine Blue 3pp. (1988)] **PEER REVIEWED***

Persistence/Bioaccumulation: 3

[HSDB] TERRESTRIAL FATE: …Pigment Blue 15 is expected to absorb to soils(SRC). Volatilization from moist soil surfaces is not expected to be an important fate process as this compound is a chelate, which tend to be stabile in the environment(2,4). Pigment Blue 15 is not expected to volatilize from dry soil surfaces(SRC) based upon an estimated vapor pressure of 3.2X10-19 mm Hg at 25 deg C(SRC), determined from a fragment constant method(5). A 0% of theoretical BOD using activated sludge in the Japanese MITI test(6) suggests that biodegradation of Pigment Blue 15 in the environment may be limited(SRC).
*[(1) O'Neil MJ, ed; The Merck Index. 15th ed. Whitehouse Station, NJ: Merck and Co., Inc. p. 423 (2006) (2) Baughman GL, Perenich TA; Amer Dyestuff Reporter p. 19-22. February (1988) (3) Evans LJ; Environ Sci Technol 23: 1046-56 (1989) (4) Snoeyink VL, Jenkins D; Water Chemistry. New York, NY: John Wiley & Sons, p. 202 (1980) (5) Lyman WJ; p. 31 in Environmental Exposure From Chemicals Vol I, Neely WB, Blau GE, eds, Boca Raton, FL: CRC Press (1985) (6) NITE; Chemical Risk Information Platform (CHRIP). Biodegradation and Bioconcentration. Tokyo, Japan: Natl Inst Tech Eval. Available from, as of April 20, 2010: http://www.safe.nite.go.jp/english/db.html**PEER REVIEWED***

[HSDB] AQUATIC FATE: …Pigment Blue 15 is expected to absorb to aquatic soils and sediments(SRC). It is not expected to undergo volatilization(2) as this compound is a chelate, which tend to be stabile in the environment(4). According to a classification scheme(5), experimental BCF values of less than 0.33 to 11 (test concentration = 0.6 mg/L) and less than 3.6 (test concentration = 0.06 mg/L)(6), suggest the potential for bioconcentration in aquatic organisms is low(SRC). A 0% of theoretical BOD using activated sludge in the Japanese MITI test(6) suggests that biodegradation of Pigment Blue 15 in the environment may be limited(SRC).
*[(1) O'Neil MJ, ed; The Merck Index. 15th ed. Whitehouse Station, NJ: Merck and Co., Inc. p. 423 (2006) (2) Baughman GL, Perenich TA; Amer Dyestuff Reporter p. 19-22. February (1988) (3) Evans LJ; Environ Sci Technol 23: 1046-56 (1989) (4) Snoeyink VL, Jenkins D; Water Chemistry. New York, NY: John Wiley & Sons, p. 202 (1980) (5) Franke C et al; Chemosphere 29: 1501-14 (1994) (6) NITE; Chemical Risk Information Platform (CHRIP). Biodegradation and Bioconcentration. Tokyo, Japan: Natl Inst Tech Eval. Available from, as of April 20, 2010: http://www.safe.nite.go.jp/english/db.html **PEER REVIEWED***

[PHAROS] Persistent [EC - CEPA DSL]

Aquatic toxicity/ecotoxicity: 1

[PHAROS] Non-Hazardous to Water [German FEA - Water Hazard Class 0 NWG]

[HSDB] LC50; Species: Oryzias latipes (Orange-red killifish); Conditions: static; Concentration: >100 mg/L for 48hr (reported as 100 ppm w/v)
*[Organization for Economic Cooperation and Development; Screening Information Data Set for Copper phthalocyanine, CAS #147-14-8 p.146 (1993). Available from, as of April 27, 2010: http://www.chem.unep.ch/irptc/sids/OECDSIDS/sidspub.html **PEER REVIEWED** [HSDB]*

[HSDB] LC50; Species: Coryza sativa (rice) Toyonishiki; Conditions: OECD Guideline. Test substance practically insoluble; Concentration: >100 mg/L (reported as >100 ppm w/v)
*[Organization for Economic Cooperation and Development; Screening Information Data Set for Copper phthalocyanine, CAS #147-14-8 p.147 (1993). Available from, as of April 27, 2010: http://www.chem.unep.ch/irptc/sids/OECDSIDS/sidspub.html **PEER REVIEWED** [HSDB]*

[HSDB] LC50; Species: Brassica rapa Hikari (turnip); Conditions: OECD Guideline. Practically insoluble. The substance stained the roots of the test plant at concentration of 100 mg/L; Concentration: >100 mg/L (reported as >100 ppm w/v);
*[Organization for Economic Cooperation and Development; Screening Information Data Set for Copper phthalocyanine, CAS #147-14-8 p.147 (1993). Available from, as of April 27, 2010: http://www.chem.unep.ch/irptc/sids/OECDSIDS/sidspub.html **PEER REVIEWED** [HSDB]*

[HSDB] LC50; Species: Lettuca sativa (lettuce); Conditions: OECD Guideline. Practically insoluble. The substance stained the roots of the test plant at concentration of 100mg/L; Concentration: >100 mg/L (reported as >100 ppm w/v)
*[Organization for Economic Cooperation and Development; Screening Information Data Set for Copper phthalocyanine, CAS #147-14-8 p.148 (1993). Available from, as of April 27, 2010: http://www.chem.unep.ch/irptc/sids/OECDSIDS/sidspub.html **PEER REVIEWED** [HSDB]*

Acute Toxicity: 1

[HSDB] LD50 Rat oral > 10,000 mg/kg bw
*[Organization for Economic Cooperation and Development; Screening Information Data Set for Copper phthalocyanine, CAS #147-14-8 p.134 (1993). Available from, as of April 27, 2010: http://www.chem.unep.ch/irptc/sids/OECDSIDS/sidspub.html **PEER REVIEWED***

[HSDB] LD50 Rabbit oral 16,000 mg/kg bw
*[Organization for Economic Cooperation and Development; Screening Information Data Set for Copper phthalocyanine, CAS #147-14-8 p.134 (1993). Available from, as of April 27, 2010: http://www.chem.unep.ch/irptc/sids/OECDSIDS/sidspub.html **PEER REVIEWED***

[HSDB] May cause eye irritation. May cause skin irritation. May cause respiratory tract irritation.
[Sigma-Aldrich Corp; Safety Data Sheet for Copper(II) phthalocyanine (Product Number:

*546682) Version 3.0 (December 29, 2008). Available from, as of June 15, 2010: http://www.sigmaaldrich.com **PEER REVIEWED***

[SDS] LD50 oral rat >2000mg/kg
[SDS] LD50 dermal rat > 5000mg/kg
[SDS] rabbit – no skin irritation 4 h
[SDS] rabbit – no eye irritation 24 h

Chronic Toxicity: 1

[HSDB] LABORATORY ANIMALS: Subchronic or Prechronic Exposure/ 13 week feeding study in mice with dosage of 5,000 mg/kg bw/day. Results: no toxic signs or pathological changes were found after 13 weeks of testing.
*[Organization for Economic Cooperation and Development; Screening Information Data Set for Copper phthalocyanine, CAS #147-14-8 p.135 (1993). Available from, as of April 27, 2010: http://www.chem.unep.ch/irptc/sids/OECDSIDS/sidspub.html **PEER REVIEWED***

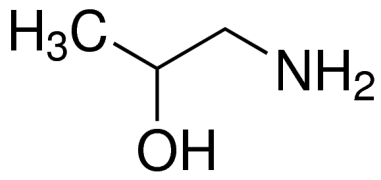
LABORATORY ANIMALS: Subchronic or Prechronic Exposure/ 28 day repeated dose toxicity test with dose levels of 0, 40, 200, and 1,000 mg/kg per day administered by oral gavage, SLC Wistar rats, 10 male and 10 female per group…Estimated dose of low concern for repeated dose toxicity in rats was calculated as 0.2mg/kg per day.
*[Organization for Economic Cooperation and Development; Screening Information Data Set for Copper phthalocyanine, CAS #147-14-8 p.135-6 (1993). Available from, as of April 27, 2010: http://www.chem.unep.ch/irptc/sids/OECDSIDS/sidspub.html **PEER REVIEWED** [HSDB]*

LABORATORY ANIMALS: Subchronic or Prechronic Exposure/ In a 13-week feeding study of rats and mice conducted by the NTP, no signs of toxicity were reported at dosage levels of 0.3% to 5% in food.
*[Organization for Economic Cooperation and Development; Screening Information Data Set for Copper phthalocyanine, CAS #147-14-8 p.135-6 (1993). Available from, as of April 27, 2010: http://www.chem.unep.ch/irptc/sids/OECDSIDS/sidspub.html **PEER REVIEWED** [HSDB]*

OTHER

[PHAROS] Verified Low Concern [US EPA - DfE SCIL - Green Circle]

1-amino-2-propanol [78-96-6]



Carcinogenicity/ Mutagenicity: Data Gap

Endocrine disruptor/Reproductive toxicity/ Developmental toxicity: Data Gap

Sensitization: Data Gap

Persistence/Bioaccumulation: 2

[HSDB] TERRESTRIAL FATE: Based upon an estimated Koc of 7.1, 1-amino-2-propanol is expected to leach readily in soil(4,SRC). The importance of leaching may be lessened by concurrent biodegradation. Based upon a vapor pressure of 0.47 mm Hg at 25 deg C(5), 1-amino-2-propanol should evaporate slowly from dry surfaces(SRC).
*[(1) Bridie AL et al; Water Res 13: 627-30 (1979) (2) Ettinger MB; Ind Eng Chem 48: 256-9 (1956) (3) Chou WL et al; Biotechnol Bioeng Symp 8: 391-414 (1979) (4) Lyman WJ et al; Handbook of Chemical Property Estimation Methods NY: McGraw-Hill p. 4-9 (1982) (5) Daubert TE, Danner RP; Physical and Thermodynamic Properties of Pure Chemicals: Data Compilation, NY: Hemisphere Pub Corp (1989)] **PEER REVIEWED***

[HSDB] AQUATIC FATE: The dominant removal process for 1-amino-2-propanol in water is expected to be biodegradation. Several biodegradation studies have demonstrated that 1-amino-2-propanol is readily biodegradable(1,2,3). Aquatic volatilization, bioconcentration, and adsorption to sediment are not expected to be important(SRC).
*[(1) Bridie AL et al; Water Res 13: 627-30 (1979) (2) Ettinger MB; Ind Eng Chem 48: 256-9 (1956) (3) Chou WL et al; Biotechnol Bioeng Symp 8: 391-414 (1979)] **PEER REVIEWED***

[HSDB] In anaerobic serum bottle degradation studies, 1-amino-2-propanol exhibited a lag period of 9 days followed by a removal rate of 22 mg/l/day(3); during the observation period, 65% of initial 1-amino-2-propanol was removed compared to 100% removal for 1-propanol(3).
*[(1) Bridie AL et al; Water Res 13: 627-30 (1979) (2) Ettinger MB; Ind Eng Chem 48: 256-9 (1956) (3) Chou WL et al; Biotechnol Bioeng Symp 8: 391-414 (1979) (4) Speece RE; Environ Sci Technol 17: 416A-27A (1983)] **PEER REVIEWED***

Aquatic toxicity/ecotoxicity: 1

[PHAROS] German FEA – low hazard to waters Class 1

Acute Toxicity: 3

[PHAROS] Australia GHS H302: harmful if swallowed

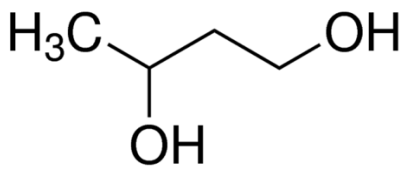
LD50 Rat oral 4.26 g/kg
*[Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983., p. 777] **PEER REVIEWED***

[PHAROS] EU & Australia GHS H314 Causes sever skin burns and eye damage, NZ GHS 8.2C Corrosive to dermal tissue, EU R34 causes burns, Australia GHS H312 Harmful in contact with skin

[HSDB] Isopropanol amine rated 7-9 on rabbit eyes. ... Tested externally on eyes of rabbits & ... Rated numerically on scale of 1-10 according to degree of injury ... After 24 hr /observation/, paying particular attention to condition of cornea. Most severe injuries have been rated 10.
*[Grant, W. M. Toxicology of the Eye. 2nd ed. Springfield, Illinois: Charles C. Thomas, 1974., p. 1161] **PEER REVIEWED***

[PHAROS] Eye Irritation – NZ GHS 8.3A Corrosive to ocular tissue

Butylene Glycol [107-88-0]



Carcinogenicity/Mutagenicity: 1

[EPA ACToR] Not genotoxic in an endogenous gene animal assay and multiple bacterial assays

Endocrine disruptor/Reproductive toxicity/ Developmental toxicity: 2

[EPA ACToR] No effect on insulin levels in a study with goats
[EPA ACToR] Decreased milk production in cows
[EPA ACToR] No effect on ovaries or pituitary glands in rats
[EPA ACToR] Lowered birthweight for maternal exposure in rats at 7060 mg/kg

Sensitization: Data Gap

Persistence/Bioaccumulation: 1

[EPA ACToR] Canada Domestic Substance List – not bioaccumulative or persistent
[HSDB] Biodegradable
Miscible in water so low bioaccumulation

Aquatic Toxicity/Ecotoxicity: 1

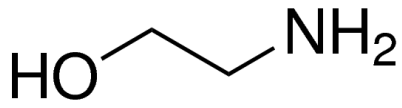
[PHAROS] German FEA Class 1 – Low Hazard to Waters
[PHAROS] Pesticide – US EPA FIFRA registered pesticide

Acute Toxicity: 1

[PHAROS] New Zealand GHS oral acute toxicity – low hazard
[PubChem] Gastrointestinal, kidney, ureter, and bladder changes in guinea pig at 11 g/kg

[EPA ACToR] Causes severe stinging in the human eye
[EPA ACToR] Not irritating to skin or mucous membranes

Ethanol Amine [141-43-5]



Carcinogenicity/Mutagenicity: 2

[EPA ACToR] Negative mutagenicity tests in multiple bacterial assays
[HSDB] weak inducer of chromosome breaks

Endocrine disruptor/Reproductive toxicity/ Developmental toxicity: 2

[PHAROS] Low pregnancy risk, MAK Group C
[EPA ACToR] Teratogen, University of Maryland chemical hygiene plan

Sensitization: 4

[PHAROS] Asthmagen, AOEC
[PHAROS] Skin sensitizer, Category 1, Japan
[PHAROS] German MAK danger of skin sensitization
[PHAROS] Quebec CSST agent causing occupational asthma

Persistence/Bioaccumulation: 1

[EPA ACToR] Aqueous solvent chemical, low environmental persistence, EPA OPPT
[HSDB] Biodegradable
[HSDB] Bioaccumulation is low

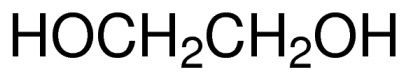
Aquatic Toxicity/Ecotoxicity: 2

[PHAROS] Hazardous to the aquatic environment, Category 2, Japan GHS, New Zealand GHS
[EPA ACToR] Moderate ecological toxicity, EPA OPPT
[PHAROS] German FEA – Class 1 – Low Hazard to waters

Acute Toxicity: 3

[PHAROS] Acutely toxic, New Zealand GHS
[PHAROS] Specific target organs and systemic toxicity, Japan GHS Category 1
[PHAROS] Severe skin burns and eye damage, EU, New Zealand, Japan, and Australia GHS
[PHAROS] Eye damage, Category 1, New Zealand and Japan GHS

Ethylene Glycol [107-21-1]



Carcinogenicity/Mutagenicity: 2

[EPA ACToR] Mutagen, UMD Chemical hygiene plan
[EPA ACToR] Negative results, mouse studies

NTP technical report on the toxicology and carcinogenesis studies of ethylene glycol (CAS no. 107-21-1) in B6C3F́ mice (feed studies)

Endocrine disruptor/Reproductive toxicity/ Developmental toxicity: 2

[PHAROS] Some evidence of no adverse effects, US NIH
[PHAROS] Low pregnancy risk, MAK Group C
[PHAROS] Clear evidence of adverse effects, CA EPA

Potential endocrine disruptor, TEDX
Potential activity listed on the endocrine disruption exchange
"Endocrine-Disrupting Activity of Hydraulic Fracturing Chemicals and Adverse Health Outcomes After Prenatal Exposure in Male Mice" http://dx.doi.org/10.1210/en.2015-1375#sthash.1W0yb9Kd.dpuf

Sensitization: Data Gap

Persistence/Bioaccumulation: 1

[EPA ACToR] Water soluble

Aquatic Toxicity/Ecotoxicity: 2

[PHAROS] Low hazards to water, German FEA Class 1
[PHAROS] Registered pesticide, US EPA FIFRA
[PHAROS] Hazardous air pollutant, US EPA

Acute Toxicity: 3

[PHAROS] Organ toxicant, NZ and Japan GHS Category 1

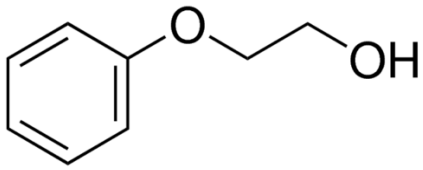
- H372: Causes damage to organs through prolonged or repeated exposure [Danger Specific target organ toxicity, repeated exposure - Category 1]

[PHAROS] Harmful if swallowed, EU, Quebec, Japan, NZ, Australia

Many other sources for acute toxicity if swallowed – but this is not a huge concern based on use of compound

[PHAROS] Skin irritation, Japan GHS Category 2
[PHAROS] May cause resp. irritation, Japan GHS Category 3
[PHAROS] Harmful if inhaled, Japan GHS Category 4
[PHAROS] Eye irritation, Japan and NZ Category 2

Phenoxy Ethanol [122-99-6]



Carcinogenicity/Mutagenicity: 1

[EPA ACToR] Not genotoxic in multiple bacterial assays

Reproductive/Developmental Toxicity: 2

[PHAROS] Suspected human reproductive toxicant, NZ GHS
[PHAROS] Low pregnancy risk, MAK Group C

Sensitization: Data Gap

Persistence/Bioaccumulation: 1

[EPA ACToR] Readily biodegradable, OECD
[HSDB] Low bioaccumulation

Aquatic/Ecotoxicity: 2

[PHAROS] Low hazards to water, German FEA Class 1
[PHAROS] Terrestrial ecotoxicant, NZ GHS

Acute Toxicity: 2

[PubChem] Brain degenerative damage in mouse and rat studies
[PubChem] Gastrointestinal, kidney, ureter, and bladder changes in rat studies
[PHAROS] NZ 6.1D dermal/inhalation/oral
[PHAROS] EU+Aus harmful if swallowed
[PHAROS] Eye irritation, Japan and NZ Category 2, EU, Australia

Appendix II: Additional Strategy Resources

Less hazardous colorants – torrefied walnut shells

Torres, L. (2016, November 10). Personal Interview.

Snowdon, M. R., Mohanty, A. K., & Misra, M. (2014). A Study of Carbonized Lignin as an Alternative to Carbon Black. *ACS Sustainable Chemistry & Engineering*, *2*(5), 1257–1263. http://doi.org/10.1021/sc500086v

Gonugunta, P., Vivekanandhan, S., Mohanty, A. K., & Misra, M. (2012). A Study on Synthesis and Characterization of Biobased Carbon Nanoparticles from Lignin. *World Journal of Nano Science and Engineering*, *02*(03), 148–153. http://doi.org/10.4236/wjnse.2012.23019

Polypropylene grafting with maleic anhydride

Bettini, S.H.P., Agnelli, J.A.M. "Grafting of Maleic Anhydride onto Polypropylene by Reactive Extrusion" Journal of Applied Polymer Science, Vol. 85 2706-2717 (2002).

Minoura, Y., Ueda, M., Mizunuma, S., & Oba, M. (1969). The reaction of polypropylene with maleic anhydride. *Journal of Applied Polymer Science*, *13*(8), 1625–1640. http://doi.org/10.1002/app.1969.070130805

Polypropylene binding peptides

Adey, N. B., Mataragnon, A. H., Rider, J. E., Carter, J. M., & Kay, B. K. (1995). Characterization of phage that bind plastic from phage-displayed random peptide libraries. *Gene*, *156*(1), 27–31. http://doi.org/10.1016/0378-1119(95)00058-E

Murray, C., Tijerina, P., Estell, D., & Chen, Y. (2004). Methods for selective targeting. US Patent Office.

O'Brien, J., & Yang, J. (2004). Peptide-based diblock and triblock dispersants and diblock polymers. US Patent Office.

Grinstaff, M., Kenan, D., & Walsh, E. (2002). Interfacial biomaterials. US Patent Office.

Cheng, Q., Fahnestock, S. R., He, H., & Kostichka, K. N. (2014). Peptide linkers for effective multivalent peptide binding. US Patent Office.

Funk, C., Schroeder, W. P., Napiwotzki, A., & Tjus, S. E. (1995). The PSII-S protein of higher plants: a new type of pigment-binding protein. *Biochemistry*, *34*(35), 11133–11141. http://doi.org/10.1021/bi00035a019