

Dangerous Waste Guidance for Pre-Impregnated Resin Composites

Hazardous Waste and Toxics Reduction Program

Washington State Department of Ecology Olympia, Washington

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¹ www.ecology.wa.gov/contact

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Northwest Region 206-594-0000 Central Region 509-575-2490 Eastern Region 509-329-3400

Region	Counties served	Mailing Address	Phone
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Northwest	Island, King, Kitsap, San Juan, Skagit, Snohomish, Whatcom	P.O. Box 330316 Shoreline, WA 98133	206-594-0000
Central	Benton, Chelan, Douglas, Kittitas, Klickitat, Okanogan, Yakima	1250 West Alder Street Union Gap, WA 98903	509-575-2490
Eastern	Adams, Asotin, Columbia, Ferry, Franklin, Garfield, Grant, Lincoln, Pend Oreille, Spokane, Stevens, Walla Walla, Whitman	4601 North Monroe Spokane, WA 99205	509-329-3400
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Introduction

Prepreg is widely used in the advanced composite industry—most often in aircraft and aerospace sectors. It's also used in the automotive and recreation industries.

Prepreg refers to fiber materials, often carbon, graphite, or glass fiber that comes "pre-impregnated" with resins or epoxies and a curing agent. This resin or epoxy and fiber mixture, once cured, reinforces the strength of the final product. Until it cures, prepreg is flexible and molds to any shape. To keep prepreg from curing prematurely, the fabric must be stored in a refrigerator or freezer.

Prepreg stored in a refrigerator or freezer is referred to as **B-Stage** or **uncured**. Prepreg that has hardened, through either heating or being left out of a refrigerator, is considered **cured**.

Prepreg waste may designate as dangerous waste in Washington State. Ecology has developed this guidance and the <u>Interim Policy for Prepreg Waste</u>³ to clarify allowable practices and improve consistency due to some challenges with management and designation. Facilities that meet the Interim Policy conditions can choose to manage their prepreg waste under the policy rather than the Dangerous Waste Regulations (Chapter 173-303 WAC).

Designating Prepreg Waste

This guide covers designation topics that are specific to prepreg waste under common conditions. Your waste may be different. You are required to fully designate your waste by following all of the steps outlined in the Dangerous Waste Regulations. Each point of generation for different types of prepreg waste must be designated as a separate waste stream.

Listed Waste

Prepreg waste is not typically a listed waste. Listed wastes have waste codes P, U, F, or K. See WAC 173-303-080 for more details.

Characteristic Waste

Prepreg waste does not typically have the physical properties to qualify as dangerous waste under the characteristics of ignitability, corrosivity, reactivity, or toxicity. See WAC 173-303-090 for more details.

State-only Criteria for Toxicity or Persistence

Prepreg waste may qualify as dangerous waste for state-only toxicity or persistence. See WAC 173-303-100 for more details.

Prepreg waste can be designated by using book designation and generator knowledge or by using analytical methods. Current test methods for persistence may detect halogens present in

³ https://apps.ecology.wa.gov/publications/SummaryPages/1804029.html

the prepreg waste, but these halogenated compounds might not meet the definition of persistence. The halogens may also be present as a polymer and qualify for the polymer allowance.

A more detailed discussion on how to determine if prepreg designates under our state criteria is included under the <u>State Only Designation Criteria section</u> of this guidance document. To learn more about designation, please read our <u>Designating Dangerous Waste publication</u>⁴ or visit our <u>Designate your waste</u> — is it dangerous? webpage.⁵

Curing Prepreg Dangerous Waste

Uncured prepreg stored at ambient conditions during accumulation or transportation can create potentially unsafe conditions due to the heat prepreg material generates as it cures naturally. The intention for curing is to reduce the physical hazards of pressure and fire if the waste is stored in a sealed container. Ecology allows generators to cure dangerous waste prepreg in their process ovens without needing a treatment, storage, and disposal (TSD) permit.

Generators can take advantage of this on-site **curing allowance** as long as all criteria below are met:

- Prepreg that is heat-cured according to manufacturer specifications is considered fully cured when managed under the <u>Interim Policy for Prepreg Waste</u>.⁶ The oven used to cure the prepreg waste must:
 - o Be the same oven used to cure the prepreg product on site.
 - Be operated at the same temperature, pressure, and relative time scale as the prepreg product is subject to.
 - Not be used to incinerate, destroy, or burn for energy recovery.⁷
 - Comply with all applicable air quality regulations, including all required permits from the local air authority or Ecology's Air Program for prepreg materials.
- The generator only cures their own waste on site. A generator cannot cure waste from other facilities.

Recycling Prepreg

Off-spec prepreg sheets or rolls, cut ends, or other scrap materials may be recycled. If these recyclable materials are recycled directly into usable products or as ingredients in a process to make a product without reclamation, they may be conditionally exempt from dangerous waste regulations under WAC 173-303-017(2).8

⁴ https://apps.ecology.wa.gov/publications/SummaryPages/96436

⁵ ecology.wa.gov/designation

⁶ https://apps.ecology.wa.gov/publications/SummaryPages/1804029.html

⁷ While being cured in the oven, the lid can be off of the waste container.

⁸ http://app.leg.wa.gov/WAC/default.aspx?cite=173-303-017

For example, uncured prepreg scraps can be used as an ingredient to make new prepreg sheets, which can then be turned into new composite products.

The generator is responsible for ensuring the recycling process is legitimate and meets the terms of WAC 173-303-017(2).

Reclaiming Prepreg

Scrap prepreg that is reclaimed remains a solid waste per WAC 173-303-017(1), and subject to the recycling requirements of WAC 173-303-120. Dangerous waste prepreg used to make products that contact the ground also remain a solid waste. Recycling may still be an option under applicable rules in WAC 173-303-505.

Prepreg reclamation processes include separation of carbon fibers from prepreg waste by chemical or pyrolysis processes. Reclamation usually involves additional regulatory requirements and possible dangerous waste permitting:

- Recycling facilities reclaiming dangerous waste are regulated as dangerous waste recyclers under <u>WAC 173-303-120(3)</u> and (4)⁹ and may need a dangerous waste storage permit.
- Generators using a dangerous waste recycler must manage the recyclable materials as a dangerous waste, including on-site dangerous waste management and shipment on a dangerous waste manifest.

Please contact Ecology's Hazardous Waste and Toxics Reduction Program to learn more about this topic.

On-site Prepreg Waste Accumulation Safety Hazards

When prepreg waste cures and hardens on its own, it can generate a significant amount of heat. The heat generated by natural-curing prepreg waste inside a lidded container (the typical compliance standard) can create enough internal pressure that the container fails or bursts.

This poses a possible physical safety hazard. Because of this hazard, Ecology will not require a complete seal on prepreg container lids to allow adequate release of built-up heat. Other satellite accumulation area and 90/180 day accumulation area standards apply.

State-only Dangerous Waste Designation Criteria

Washington State has state-only criteria requirements to help protect the environment and human health. To determine if your prepreg waste designates as a state-only waste, you will need to evaluate the waste as a whole by looking at the waste's chemical components.

⁹ http://app.leg.wa.gov/WAC/default.aspx?cite=173-303-120

Washington <u>state-only criteria</u> ¹⁰ that you must evaluate prepreg waste for include:

- Toxicity (waste codes WT01 or WT02).
- Persistence (waste codes WP01, WP02, and WP03).

To determine if a waste meets toxicity and persistence criteria for Washington State, check the regulations (WAC 173-303-100) and:

• Book designate your waste if you have data through Safety Data Sheets, Technical Data Sheets, and other manufacturer information.

OR

- Conduct analytical testing, if available and appropriate for your waste stream. Recommended analytical methods are discussed later in this section.
 - o If you cannot determine the chemical makeup of the waste, consult with a lab:
 - Refer to Sampling, testing methods, and analytes (WAC 173-303-110).¹¹
 - For Ecology approved analytical methods, refer to:
 - Chemical Test Methods for Designating Dangerous Waste.¹²
 - <u>Biological Testing Methods for the Designation of Dangerous</u>
 Waste.¹³

If you cannot find information for a chemical or need assistance, please <u>contact your regional</u> compliance inspector or toxics reduction staff.¹⁴

State-only Toxicity Criteria

You can designate prepreg waste for state toxicity in one of two ways:

- Book Designation.
- Fish Bioassay.

Book Designation

When you know what's in your waste, you can use a process called "book designation" to designate your waste for Washington state-only toxicity. In this process, you look up reasonably available test data for each chemical in your waste to determine how toxic it is to fish and animals.

¹⁰ ecology.wa.gov/StateOnlyDW

¹¹ http://apps.leg.wa.gov/WAC/default.aspx?dispo=true&cite=173-303-110

¹² https://apps.ecology.wa.gov/publications/SummaryPages/97407

¹³ https://apps.ecology.wa.gov/publications/SummaryPages/8012

¹⁴ ecology.wa.gov/contact.html

Follow the process outlined below, using WAC 173-303-100(5)(b) as a reference. 15

For each chemical in prepreg waste:

- Obtain all relevant Safety Data Sheets (SDS).
- Assign a toxic category to each chemical.
- Calculate the equivalent dangerous waste concentration of your prepreg waste to determine if the waste designates for Washington state-only toxicity.

If you are unable to determine toxicity through book designation, you must analyze using a fish bioassay. To learn more about designation, please read our <u>Designating Dangerous Waste</u> publication¹⁶ or visit our <u>Designate</u> your waste — is it dangerous? webpage.¹⁷

Fish Bioassay

This test is described in our <u>Biological Testing Methods for the Designation of Dangerous Waste</u> publication.¹⁸

State-only Persistence Criteria

Prepreg waste can be designated for state persistence in one of two ways:

- Applying designation knowledge.
- Analytical Test Methods.

Generators may use additional information to determine whether State-only persistence criteria applies to their scrap prepreg. The common reasons that State-only persistence would not apply include:

- The material does not meet the definition of persistence.
- The material meets the Polymer Allowance (as described later in this guidance).

Persistence Definition

Persistence is defined under <u>Definitions</u> (WAC 173-303-040)¹⁹ as:

"The quality of a material that retains more than half of its initial activity after one year (365 days) in either a dark anaerobic or dark aerobic environment at ambient conditions."

Some halogenated organic compounds (HOC) or polycyclic aromatic hydrocarbons (PAH) meet the definition of persistence. Some of these compounds may be found in prepreg products.

¹⁵ http://apps.leg.wa.gov/WAC/default.aspx?dispo=true&cite=173-303-100

¹⁶ https://apps.ecology.wa.gov/publications/SummaryPages/96436

¹⁷ ecology.wa.gov/designation

¹⁸ https://apps.ecology.wa.gov/publications/SummaryPages/8012

¹⁹ http://apps.leg.wa.gov/WAC/default.aspx?dispo=true&cite=173-303-040

Applying Designation Knowledge

State-only persistence can be determined by the presence of PAHs or HOCs that meet the definition of persistence.

HOCs are present in many prepreg materials.²⁰ These are:

"...organic compounds...[that]...include one or more atoms of fluorine, chlorine, bromine, or iodine...bonded directly to a carbon atom."

For example, methylene chloride (dichloromethane or DCM) is an example of a simple HOC because it has two chlorine atoms connected to a carbon atom as shown in the below image:

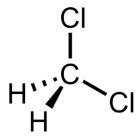


Figure 1. Dichloromethane molecular structure²¹

To check if your prepreg waste meets persistence criteria, evaluate each compound. You will need complete ingredient information for all of your prepreg waste. You can find this information through:

- Safety Data Sheets (SDS).
- Manufacturer information.

Once you know the HOCs present in your prepreg waste, determine which HOCs meet persistence criteria:

- Evaluate each HOC against the persistence definition.
 - Ensure you are accounting for all HOCs present in the waste stream and evaluating them separately. A complete ingredient list is needed for each prepreg material to ensure all HOC compounds are evaluated.
 - U.S. National Library of Medicine's Toxicology Data Network (TOXNET)²² and Environmental Protection Agency's (EPA's) Chemical Dashboard²³ are available technical resources to assist in making this determination.

²⁰ See WAC 173-303-040 for full regulatory definitions of HOC and PAH.

²¹ Ohnodoctor, 2016. This work is licensed under a Creative Commons Attribution-ShareAlike 4.0 International License (https://creativecommons.org/licenses/by-sa/4.0/). No changes were made to the original image. https://commons.wikimedia.org/wiki/File:Dichloromethane molecular structure.png.

²² https://www.nlm.nih.gov/toxnet/index.html

²³ epa.gov/chemical-research/chemistry-dashboard

- Retain technical resources used to evaluate and make them available for review by inspectors.
- For all HOCs that meet persistence criteria, you must:
 - Use one of the methods below to verify the amount present in your prepreg waste.
 - Total the concentration of HOC compounds in your prepreg waste to show how it should designate.

Prepreg waste designates as dangerous waste if the total concentration of HOC compounds is:

- Greater than 10,000 ppm (parts per million) or 1%.²⁴ The waste designates as a **WP01** dangerous waste and is an extremely hazardous waste (EHW).
- Greater than 100 ppm or 0.01% and less than 10,000 ppm or 1%. The waste designates
 as a WP02 dangerous waste and may also be managed as a special waste (see special
 waste section).

If you do not know the percent by weight of each HOC then you will need to use a test method to determine proper designation. Manufacturers or suppliers may be able to provide this information.

Analytical Test Methods

There are several approved analytical test methods for determining if your waste contains halogenated compounds.

There are different test methods you can use to detect halogens in prepreg waste. The choice of test method depends on the type of HOCs in the waste. Contact the manufacturer or supplier to find out which ones are in your prepreg material.

If the types of HOCs are unknown, or you do not know the percent by weight of each known HOC, then we recommend using one of the below test methods to determine total halogen content.²⁵ If you know the HOCs present, you can tailor these test methods to focus only on those halogens. If multiple test methods are run on a particular waste stream, individual organic halide concentrations need to be summed up to get the total organic halogen concentration.

EPA Method 9023

<u>EPA Method 9023 (Extractable Organic Halides in Solids)</u>²⁶ is used to determine total extractable organic halides, including chlorine, bromine, or iodine. This test method is prepared via acidic extract followed by pyrolysis and microcoulometric titration.

²⁴ To determine the percent HOC in your waste, sum up the percent by weight of each HOC.

²⁵ Read Chemical Test Methods for Designating Dangerous Waste (Ecology publication 97-407) for more information about the methods described in this section:

https://apps.ecology.wa.gov/publications/SummaryPages/97407.html.

²⁶ https://www.epa.gov/hw-sw846/sw-846-test-method-9023-extractable-organic-halides-eox-solids

- This test does not detect fluorine.
 - If fluorinated compounds are in the waste, this method may underestimate the total halogens present.
 - Use EPA Methods 5050 and 9056 if you expect fluorine-containing additives are in the prepreg.
- It can be modified for high molecular weight HOCs. High molecular weight HOCs (such as polybrominated diphenyl ethers [PBDEs]), which are common flame retardants, are difficult to extract using the standard ethyl acetate extraction method. Your lab may be able to modify the extraction solvent to suit high molecular weight wastes.

EPA Methods 5050 and 9056a

<u>EPA Method 5050 (Bomb Preparation)</u>²⁷ is used in conjunction with <u>EPA Method 9056a</u> (<u>Determination of Inorganic Anions by Ion Chromatography</u>)²⁸ to determine fluorine, chloride, and bromine halogen content.

- The test method does not detect iodine. If iodine compounds are in the waste, this
 method may underestimate the total halogens present. This test detects fluorine,
 chloride, and bromine separately. They can be summed up to determine the total
 halogen content.
- It may detect inorganic halogens. The presence of inorganic halogens could affect designation. We do not regulate inorganic halogens. If you choose, you can conduct further analysis to prove the waste is not persistent.
- Always use Method 5050 as a preparatory method. This method makes halogen anions available for analysis by combusting the waste to an ash. Verify your laboratory is equipped to perform the bomb preparation method.

Polymer Allowance

Ecology does not intend to regulate halogenated polymers as dangerous waste. Polyvinyl chloride (PVC) and neoprene are examples of halogenated polymers. These do not have to be designated or managed as dangerous waste. If a waste fits the definition of a halogenated polymer, Ecology gives an allowance from the designation requirement.

See our <u>Chemical Test Methods for Designating Dangerous Waste publication</u>, ²⁹ Chapter 2 Section 2.2.3.3 and Chapter 3 Section 3.8.6.2 for additional information on the polymer allowance.

Unpolymerized HOCs do not qualify as a halogenated polymer and still require designation prior to disposal.

²⁷ https://www.epa.gov/hw-sw846/sw-846-test-method-5050-bomb-preparation-method-solid-waste

²⁸ https://www.epa.gov/hw-sw846/sw-846-test-method-9056a-determination-inorganic-anions-ion-chromatography

²⁹ https://apps.ecology.wa.gov/publications/SummaryPages/97407

Generators must have documentation that a specific waste meets the polymer allowance. Ecology inspectors may ask for this documentation during compliance inspections as a part of the designation paperwork. (See the "Documentation" section below)

Additive Versus Reactive Compounds in Prepreg Materials

Prepreg materials often have HOC ingredients. These compounds are considered either **additive compounds** if blended or **reactive compounds** when chemically bonded in the polymer matrix. The type of HOCs found in your prepreg materials will affect the designation status when it becomes waste.

Additive Compounds Must be Evaluated

Polymer additives³⁰ are blended into the epoxy or phenolic resin. They are not incorporated into the polymer chemical structure. Since blended HOC additives are not chemically bonded within prepreg material, they may leach and release to the environment. Therefore, prepreg materials blended with additive compounds must be evaluated against the state-only persistence criteria.

Examples of additive compounds blended with prepreg materials include, but are not limited to:

- Fillers
- Fire retardants
- Pigments
- Plasticizers
- Flow improvers
- Catalysts
- Stabilizers

Reactive Compounds are not a state Persistent waste

Reactive compounds are chemically bonded to the polymer chains within prepreg material. Although they persist for extended periods of time in the environment, they resist leaching and have less of a biological impact.

Reactive compounds³¹ in prepreg materials do not need further evaluation for state-only persistence criteria if they meet the polymer allowance. These compounds are not persistent dangerous waste.

Generators are strongly encouraged to work with their manufacturer to determine if the HOC compounds in their prepreg are "additive" or "reactive" compounds.

³⁰ Mixed with the resin polymer to provide some specific characteristic; not chemically bonded to the resin polymers; maintain their chemical structure and are evenly dispersed throughout the product.

³¹ Reactive compounds are different from the dangerous waste characteristic of "reactivity" and D003

Documentation

Generators must provide written evidence to prove their prepreg waste qualifies for the polymer allowance. Required documentation includes:

- Documenting generator knowledge (see WAC 173-303-070(3)(b)(ii)) that HOC additives in their prepreg waste are reactive compounds (e.g., not blended but chemically bonded into prepreg).
 - Ecology considers documentation of generator knowledge part of the waste designation process. For most generators, this documentation would come from their prepreg manufacturer. Ecology will not require generators to divulge proprietary information about specific chemical compounds or exact percentages, only the determination that incorporated HOCs are reactive or additive.
 - Supporting information may include safety data sheets (SDS) or chemical product specifications showing the class of HOC ingredient (such as tetrabromobysphenal A [TBBPA]), which indicates that the ingredient is a reacted polymer.
- A signed statement that shows this generated waste prepreg:
 - Meets the polymer allowance criteria, and is
 - Polymerized per product manufacturing standards.

Special Waste

Special wastes pose a relatively low risk to human health and the environment. They have reduced regulatory requirements and less expensive disposal options. Your waste may qualify as a special waste if it:

- Does not designate as federal hazardous waste under 40 CFR part 261.
- Is in a solid phase (e.g., not gaseous and does not contain liquid), and
- Meets one or more of the following:
 - State-only toxic WT02 with Equivalent Concentration equal to or less than 0.01%.
 - State-only persistent WP02 with total halogenated organic compound concentration equal to or between 0.01% and 1.0%.
 - Corrosive characteristic WSC2.
 - Listed as WPCB.

Keep Designation Records

You must keep records to show how you designated your dangerous waste. Some sources of information you use in your designation process may be:

Safety Data Sheets (SDS).

- Product specifications.
- Manufacturer information.
- Chemical test results.

A dangerous waste compliance inspector may ask for your supporting designation documentation when they visit. Keep this designation information for 5 years and available for review if requested during an inspection.