
DIRIGO
MAINE

Decabromodiphenyl Ether Flame Retardant in Plastic Pallets

A Safer Alternatives Assessment

Prepared for:

Maine Department of Environmental Protection

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STATE OF MAINE
DEPARTMENT OF ENVIRONMENTAL PROTECTION

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March 23, 2011

Senator Thomas B. Saviello, Chair
Representative James M. Hamper, Chair
Committee on Environment and Natural Resources
125th Maine State Legislature
100 State House Station
Augusta Maine 04333-0100

Dear Senator Saviello, Representative Hamper and Members of the Committee:

Enclosed please find a report on the use of flame retardants in plastic shipping pallets. The report was commissioned by the Department of Environmental Protection pursuant to *An Act to Clarify Maine's Phaseout of Polybrominated Diphenyl Ethers* (herein "the Act").[1]

Section 9 of the Act authorizes the DEP to supervise a study assessing the availability of safer alternatives to the use of decabrominated diphenyl ether (decaBDE) in shipping pallets. The Act further authorized pallet manufacturers to voluntarily fund the study, which the pallet rental company iGPS agreed to do.

Upon confirming the iGPS offer, an open solicitation of bids was issued and Pure Strategies, Inc. of Gloucester, Massachusetts was chosen to conduct the study. Pure Strategies was the only bidder, but was well qualified for the job, having previously conducted an investigation of alternatives to decaBDE in electronic enclosures and textiles.[2] The project team assembled by Pure Strategies included:

- ToxServices, a Washington DC based firm with expertise in toxicology and comparative hazard assessment; and
- Flame Retardant Associates Inc., a Washington state consulting firm in the field of polymer additives including specifically flame retardants.

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[1] PL 2009, c. 610, eff. July 12, 2010.

[2] Pure Strategies, Inc., *Decabromodiphenylether: An Investigation of Non-Halogen Substitutes in Electronic Enclosure and Textile Applications,* prepared for the Lowell Center for Sustainable Production, University of Massachusetts Lowell, April 2005.

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The enclosed final report on Pure Strategies' investigation demonstrates that there are safer alternatives to the use of decaBDE in pallets. To be considered safer, an alternative to decaBDE must meet the following criteria as established under section 7 of the Act:

> "For the purposes of this subsection, 'safer alternative' means a substitute process, product, material, chemical, strategy or any combination of these that:
>
> (1) When compared to the chemical to be replaced would reduce the potential for harm to human health or the environment or has not been shown to pose the same or greater potential for harm to human health or the environment as the chemical to be replaced;
>
> (2) Serves a functionally equivalent purpose that enables applicable fire safety standards, approvals and tests and relevant performance standards to be met;
>
> (3) Is commercially available on a national basis; and
>
> (4) Is not cost-prohibitive."[3]

Pure Strategies explored three possible strategies for substituting safer alternatives for the use of decaBDE in pallets. First, the study examined whether it might be possible to meet fire safety standards using plastic pallets without flame retardants (see chapter II of the report). Next, the study examined whether other chemical retardants could be substituted for decaBDE (see chapters III through VI). Finally, the study examined whether wood pallets are a safer option (see chapters VII and VIII). Summarized below are key findings on each of these three potential alternatives, followed by the department's conclusion on whether the alternative constitutes a safer alternative as defined in the Act.

1. **ALTERNATIVE: plastic pallets without flame retardants**. The use of chemical flame retardants in plastic pallets is a relatively recent development and has been confined almost exclusively to pallets used in the rental market. This new flame retardant usage is driven by NFPA 13, a standard for warehouse sprinkler systems promulgated by the National Fire Protection Association (NFPA).[4]

   The Pure Strategies investigation—which included conversations with staff from the NFPA, the National Fire Sprinkler Association and the Maine State Fire Marshal's office—determined that there are ways to meet the fire protection requirements of NFPA 13 without using plastic pallets made with flame retardants. Newer warehouses, for example, often are equipped with ESPR (early suppression fast response) sprinkler systems that provide adequate protection for non-flame retardant pallets. There is, in fact, a large market for such pallets.[5] Their usage, however, typically is confined to captive systems in which the pallets are used internally in a fully-protected warehouse or manufacturing site or only travel between sites owned by a single company such as is the case within the Hannaford chain of grocery stores.[6]

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[3] PL 2009. c. 610, §7, enacting 38 MRSA §1609(14)(A).

[4] National Fire Protection Association, *NFPA 13: Standard for the Installation of Sprinkler Systems* (2010).

[5] Pure Strategies, Inc., *Decabromodiphenyl Ether Flame Retardant in Plastic Pallets: A Safer Alternatives Assessment*, prepared for the Maine Department of Environmental Protection, p 42.

[6] *Id.* at 25, 42.

The situation is different in the pallet rental or "open-pool leasing" market. Leased pallets typically are not used in a captive system. Rather, they are used by manufacturers and distributors to ship products all over the county to warehouses that the manufacturer or distributor does not control. A "significant portion of these warehouses lack the required sprinkler protection systems … and are unlikely to upgrade in the near future. These warehouses can take other steps (e.g., increased aisle width; outside storage of idle pallets) to reduce the fire hazard associated with the use of plastic pallets, but adherence to such practices alone is insufficient to offset the sprinkler system limitations for the purpose of compliance with NFPA 13."[7]

DEP conclusion. Pallets containing decaBDE are used predominantly in the open-pool leasing market to ship goods to warehouses across the U.S. Some of these warehouses are equipped with fire safety systems that make the use of flame retardants unnecessary but many are not. Accordingly, plastic pallets that lack flame retardants are not appropriate for use in the open-pool leasing market and cannot be considered a safer alternative to pallets containing decaBDE.

2. **ALTERNATIVE: plastic pallets made with other chemical retardants.** DecaBDE is a halogenated flame retardant, meaning it contains bromine, one of five elements in the group of elements called halogens. Of the halogens, only bromine and chlorine are effective as flame retardants. Brominated and chlorinated flame retardants have come under increasing scrutiny in scientific and regulatory circles because of concerns surrounding the toxicity of these chemicals and their increasing presence in the environment.[8] The Maine Legislature, in section 7 of the Act, explicitly prohibited the replacement of decaBDE with a brominated or chlorinated flame retardant.[9]

   The Pure Strategies study identified seven non-halogenated chemical flame retardants that, if used in plastic pallets in lieu of decaBDE, would reduce the potential for harm to human health or the environment when compared to decaBDE. The seven chemicals are: aluminum trihydroxide; ammonium polyphosphate; ethylenediamine phosphate; magnesium hydroxide; magnesium stearate; melamine polyphosphate; and zinc borate.[10]

   Two companies—Rehrig Pacific and CHEP—have developed flame retardant plastic pallets using one of these seven chemicals. Another—Orbis—has developed a pallet made with an unidentified non-halogenated flame retardant and is in the process of arranging for the required fire testing.[11]

   The Rehrig pallet, which uses a magnesium hydroxide retardant, lacks sufficient load strength for the rental market and thus cannot be considered functionally equivalent to the pallets used in that market. The CHEP pallet, on other hand, was specifically designed for use in the rental market. It uses one of the seven chemical retardants identified as safer by Pure Strategies, although CHEP has

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[7] *Id.* at 42.

[8] Brominated flame retardants appear on the list of chemicals of high concern published by the Department of Environmental Protection under 38 MRSA §1693.

[9] See PL 2009, c. 610, §7 enacting 38 MRSA §1696(14)(B)(2).

[10] Pure Strategies *supra* n 5 at 88-90.

[11] *Id.* at 47.

yet to disclose the exact one, saying only that it is phosphorus based. CHEP began production of this new pallet last month.

DEP conclusion. The existence of the Rehrig and CHEP pallets demonstrates that plastic pallets can be made with non-halogen flame retardants that, compared to decaBDE, reduce the potential for harm to human health or the environment. Neither of these pallets, however, qualifies as a "safer alternative" under the Maine law. The Rehrig pallet falls short because it lacks sufficient load strength to serve as a functionally equivalent alternative to pallets made with decaBDE. The CHEP pallet falls short because it is brand-new to the marketplace and thus has not been demonstrated to be commercially available on a national basis or affordable to users. Given CHEP's market position as the largest pallet rental company, this new plastic pallet may become a viable alternative to decaBDE pallets in the near future assuming CHEP commits itself to production and promotion.[12]

3. **ALTERNATIVE: wood pallets.** At least two companies—CHEP and PECO—offer wood pallets for use in the open-pool leasing market, the market in which plastic pallets containing decaBDE are used. The CHEP wood pallet, in fact, is the most widely used pallet in that market;[13] wood pallet companies collectively dominate the market.[14]

   Wood pallets, in contrast to plastic pallets, are not treated with chemical flame retardants for the purpose of compliance with NFPA 13.[15] This is because, under NFPA 13, different materials are assigned different commodity classifications reflecting their fire hazard and the amount of protection required. Plastic commodities, including plastic pallets, are assigned to a higher fire hazard class than wood because plastics typically produce higher-challenge fires and therefore require sprinklers that deliver more water.

   Flame retardants are added to plastic pallets to put them on a par with wood pallets for the purpose of NFPA 13. If a manufacturer can furnish fire test data showing that its plastic pallet has a fire hazard equal to or less than wood, then no additional sprinkler protection is needed by warehouses to accommodate the use of the plastic pallet. The addition of chemical flame retardants allows manufacturers to produce pallets that pass the tests for equivalence to wood.[16]

   DEP conclusion. Wood pallets are a safer alternative to the use of pallets containing decaBDE. They do not require the use of chemical retardants, yet are equivalent to flame-retardant plastic pallets for the purposes of applicable fire safety standards. The fact that wood pallets are widely used in the open-pool leasing market to ship the same types of goods as are shipped on plastic pallets containing decaBDE demonstrates that they are functionally equivalent, commercially available and affordable to users.

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[12] *Id.* at 101-2.

[13] *Id.* at 92.

[14] *Id.* at 101.

[15] In a 2007 report examining alternatives to decaBDE, the DEP and the Maine Center for Disease Control observed that alternatives which allow flammability standards to be met without using a chemical flame are presumptively safer. See Maine Department of Environmental Protection and Maine Center of Disease Control, *Brominated Flame Retardants: Third annual report to the Maine Legislature* (January 2007), p 29.

[16] Pure Strategies *supra* n 5 at 32.

As already mentioned, section 7 of the Act explicitly prohibited the replacement of decaBDE with a brominated or chlorinated flame retardant. Section 11 requires the DEP to study the issues related to this prohibition.

The Pure Strategies report shows that the main issue in developing a safer alternative is the technological challenge of designing a pallet to meet flammability standards while maintaining the necessary physical properties for the pallet to serve its intended purpose. Developing a plastic pallet with an alternative, non-halogen flame retardant requires a significant testing and evaluation investment. Finding the right mix may involve a lengthy testing process with many uncertainties and no guarantee of success.[17]

> "To summarize, five interactive design parameters are usually of importance in designing a pallet: strength, stiffness, durability, functionality and cost. These are interactive and the trick is balancing these properties. Maximizing just one will have an impact on the others. The key to a successful flame retardant plastic pallet is to design a pallet meeting all the necessary physical properties and required flammability performance by using the proper choice of polymer resin, flame retardant system, and other additives (colorants, impact modifiers, etc.)."[18]

Notwithstanding this daunting challenge, two different non-halogen flame retardant pallets (the Rehrig and CHEP pallets mentioned above) already have been developed and pallet manufacturer Orbis is ready to begin flammability testing of another non-halogen system.[19]

In the past, the effectiveness and relatively low cost of using decaBDE to meet flammability standards for plastics has served as a disincentive to the investigation of non-halogen alternatives.[20] The changing regulatory climate, including Maine's ban on replacement of decaBDE with a brominated or chlorinated flame retardant, has shifted those incentives. We recommend the ban remain in place.

Please feel to contact us if you have any questions.

Sincerely,

Darryl Brown, Commissioner
Department of Environmental Protection

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[17] *Id.* at 64.

[18] *Id.* at 53, see also *id.* Appendix V (Polymer Range for Flame Retardant Plastic Pallets) and Appendix VI (The Cost Factor and Flame Retardant Plastic Pallets).

[19] *Id.* at 68.

[20] *Id.* at 73.

Executive Summary

Maine has taken a leading role in moving to reduce public exposure to decabromodiphenyl ether (decaBDE), a potential endocrine disruptor and persistent toxic chemical used for decades as a flame retardant in a variety of consumer and other products. In 2007, Maine passed legislation banning sales or distribution of decaBDE-containing TVs, computers, mattresses and residential upholstered furniture.[1] In 2010, Maine's legislature amended the law to also mandate a phase-out of decaBDE as a flame retardant in shipping pallets as soon as practicable, and its replacement with "safer alternatives."[2] The law explains "safer alternative" as "a substitute process, product, material, chemical, strategy or any combination of these."[3]

This study is an assessment of safer alternatives to continued use of decaBDE as a flame retardant in plastic shipping pallets. The assessment evaluates the availability of non-halogenated flame retardants to replace decaBDE, their current use or potential effectiveness in making a flame retardant plastic pallet, some cost constraints that could affect the development or adoption of non-halogenated alternatives, and their potential human health and environmental impacts compared to decaBDE. The assessment also investigates the potential to reduce the need for flame retardant plastic pallets through replacement by non-plastic pallets, or by adoption of more stringent fire protection and management methods by warehouses, distribution centers or other sites handling groceries, consumer electronics or other commodities commonly moved or stored on plastic shipping pallets.

The Market for Plastic "Grocery" Pallets and Fire Protection Requirements

Shipping pallets come in a wide variety of shapes and sizes and are used for both storing and shipping a vast array of consumer goods and industrial products throughout the U.S. each day. The dominant pallet material continues to be wood, though the use of plastic is growing, particularly in the sector of greatest concern for this study: the 40" x 48" 'grocery' pallet used for shipping and storing most rapid-turnover consumer goods such as groceries, cleaners, consumer electronics and a host of other products. The grocery pallet market comprises two significantly separate marketplaces:

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[1] 2007 Laws of Maine, c. 296, enacting 38 MRSA §§1609, sub-§§4 and 5.

[2] 2009 Laws of Maine, c. 610.

[3] Subsection 14 of 38 MRSA, section 1609.

- Pallet purchases by end users for their own use within a single site or a group of sites (sometimes called 'closed pool' or 'captive' uses) controlled and managed by the user, who can ensure that pallet characteristics and warehouse management and fire protection systems are appropriately matched; and
- 'Open-pool' leasing of pallets by manufacturers and distributors sending products to warehouses for retail stores or other companies all over the country, where the fire protection and management systems of warehouses storing products on these pallets may vary widely.

While plastic pallets play an increasing role in both settings, it is their use in 'open pool' leasing that is of greatest importance in this assessment. The National Fire Protection Association (NFPA), the organization that sets most fire protection standards for communities in Maine and the rest of the country, believes the most commonly-used plastics – both in pallets and products – present a greater risk of more severe fires than wood. As a result, it requires that either warehouses storing products on plastic pallets install and implement more stringent fire protection and management systems, or that the plastic pallets include fire retardants that reduce the fire risk they pose to the level of risk posed by wood pallets. Plastic pallets in the open-pool leasing market have almost exclusively contained decaBDE as the flame retardant, and the effort to identify safer alternatives in this study focuses on that use.

More Stringent Fire Protection and Management Standards as a "Safer Alternative"

This report examines whether adoption of more stringent fire protection and management methods by warehouses and other sites handling plastic shipping pallets could eliminate the need for the use of flame retardants in those pallets. Our investigation shows that this solution, viable in 'captive' settings for pallet use, does not currently provide an adequate safer alternative for 'open pool' pallet use. ***While there are fire safety systems and management practices for warehouses and other shipping locations that can make the use of flame retardants for plastic pallets unnecessary, these are not universally available, and do not provide a comprehensive short-term, safer alternative to use of plastic pallets with flame retardants.***

The NFPA's fire protection standards for warehouses specify sprinkler systems and best management practices for commodities, packaging and pallets that present the most severe fire risks. Warehouses that achieve these levels would provide sufficient fire protection for plastic pallets without flame retardants. Some new or modernized warehouses are built entirely with the highest protection levels, and can purchase and use plastic pallets without flame retardants.

Many warehouses, however, especially older buildings, meet only minimum NFPA protection requirements. For these warehouses, general use of plastic pallets is only feasible if the pallets are flame retardant. The three open-pool leasing companies (iGPS, CHEP, PECO) moving rapid-turnover consumer products send pallets to warehouses all over the country, a significant proportion of which are not built to the highest standards. So the use of open-pool plastic pallets without flame retardants is not currently feasible as a safer alternative to the use of plastic pallets with decaBDE.

Non-halogenated Flame Retardants or Non-Plastic Pallets as a Safer Alternative to Replace Flame Retardant Plastic Pallets with DecaBDE

To assess whether safer alternative pallets could provide the services in the open-pool leasing market currently provided by flame retardant plastic pallets with decaBDE, DEP stipulated that this study compare the decaBDE plastic pallet both with flame retardant plastic pallets using non-halogenated flame retardants[4] and “with pallets made of wood and other materials”[5] that also serve ‘grocery’ pallet customers in the open-pool leasing market.

For a plastic pallet with a non-halogenated flame retardant to be included in the comparison, it must meet two minimum tests.

- *Flame retardance*: For plastic pallets in a warehouse to be subject only to the same fire protection requirements as a wood pallet, rather than the more severe restrictions generally placed on plastic pallets due to the higher fire risk they present, NFPA requires that the pallets demonstrate, “a fire hazard that is equal to or less than wood pallets and are listed as such.”[6] While the NFPA standard does not specify what listings are acceptable, the NFPA Handbook[7] identifies two large-scale fire testing protocols – the Underwriters Laboratory UL 2335 test or

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[4] DecaBDE is a halogenated flame retardant in that it contains molecules of bromine, one of five elements in the group of elements called halogens. Of the halogens, only bromine and chlorine are effective as flame retardants. Maine law at 38 MRSA §1696(14)(B)(2) prohibits a person subject to the sales ban on deca-containing pallets from replacing the decaBDE with another halogenated flame retardant.

[5] Specifications of Work to Be Performed, Task 10.

[6] National Fire Protection Association, *NFPA 13: Standard for the Installation of Sprinkler Systems*, 2010 edition, 5.6.2.6.

[7] This provides commentary and explanation, but does not have the official standing of the NFPA standard.

the Factory Mutual FM 4996 test. These tests are expensive and complex and, as of December 2010, only two plastic pallets using non-halogenated flame retardants have passed either test.

- *Toxicity:* In order to avoid the risk that a plastic pallet might use a non-halogenated flame retardant with adverse human health and environmental impacts as severe as those of decaBDE, DEP required that, as part of this report, promising non-halogenated flame retardants be reviewed with the Green Screen hazard-based screening tool developed by Clean Production Action.[8] The Green Screen assesses a wide range of chemical impacts and generates scores of 1 (avoid, chemical of high concern[9]), 2 (use but search for safer substitutes), 3 (use, but still opportunity for improvement) or 4 (safer chemical). Of the eight non-halogenated alternative flame retardants reviewed using the Green Screen for this report, only one received a score of 1; six received a score or 2; and one received a score of 4. To be acceptable as a safer alternative for this assessment, an alternative must at least receive a score of 2.

Using these criteria, two plastic pallets with safer alternative, non-halogenated flame retardants are now in production or on the market

The following are the two plastic pallets that meet these criteria:

- Rehrig Pacific Company's 40 x 48 pallet uses a magnesium hydroxide-based flame retardant that has passed the Green Screen requirement, and the pallet is listed under UL 2335.
- CHEP's 40 x 48 plastic pallet has passed both the FM 4996 and UL 2335 tests and went into production the first week of December 2010 using a proprietary, phosphorus-based flame retardant that has passed the Green Screen requirement.

While there is at least one more company with a non-halogenated flame retardant plastic pallet waiting large-scale fire testing, its flame retardant is proprietary.

Once a plastic pallet with a non-halogenated flame retardant has passed these hurdles, companies must examine whether the pallet can meet the strength, durability and other performance requirements for use in the open pool market. Experts contributing to this report noted that the challenge making it difficult to get pallets with alternative flame

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[8] http://www.cleanproduction.org/Greenscreen.php.

[9] The score received by decaBDE.

retardants to market is one of balance: the more flame retardant the formulator has to add to the plastic polymer, the more the flame retardant may weaken the pallet's crucial performance parameters.

Almost two decades ago, the Grocery Manufacturers Association (GMA) spelled out 19 design and performance specifications for a grocery pallet. Many of these specifications are now mandatory for an open-pool pallet (e.g., that the pallet must be strong enough to hold 2,800 pounds in storage while on a rack that provides support on only two edges). This study provides a comparison of the iGPS decaBDE, the Rehrig Pacific Company pallet, the CHEP plastic pallet, and the CHEP and PECO wood pallets, against the GMA specifications.

To determine whether either of the plastic pallets with non-halogenated flame retardants or the two wood pallets would provide a "safer alternative" to continued use of plastic pallets with decaBDE, DEP established two alternative criteria for determining whether one or more of these pallets provides a "functionally equivalent" alternative to the decaBDE plastic pallet.

> *"For the purpose of the study, a pallet will be considered functionally equivalent if:*
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> - *The pallet meets the Grocery Industry Pallet Performance Specifications as set forth ... [in] the Recommendations on the Grocery Industry Pallet System,... 1992 or is capable of being manufactured to meet those standards; or*
> - *The pallet currently is used by the grocery industry or other market sectors to ship the same types of good shipped on pallets containing decaBDE."*[10]

Conclusions on "Functional Equivalence"

None of the four potential alternative pallets meets the "functional equivalence" standard under the GMA performance specification test, since none meets all of the GMA specifications.

- Both wood pallets and the CHEP plastic pallet are over 60 pounds, exceeding the "desired weight" limit of less than 50 pounds.

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[10] Task 12, DEP "Specifications of Work to Be Performed."

- The Rehrig Pacific Company pallet has a rack load capacity of 2,000 pounds, which does not meet the GMA standard of 2,800 pounds. (This pallet is sold directly to end-users who may not need the capability to carry such heavy loads).
- The bottom surface covering amount appears to be lower than the GMA-specified 60% for the iGPS pallet and both CHEP pallets, while the iGPS pallet, and possibly the CHEP wood pallet, meet the 85% coverage target for the top deck.

Without considering the ambiguous results from the surface coverage specifications, the failure of three of the pallets to meet the GMA weight limit, and of the fourth to meet the GMA rack-load strength specification means that, with respect to this criterion, none of the pallets provides a functional equivalent to the decaBDE pallet.

Under the second "functional equivalence" criterion (whether the pallet "is used by the grocery industry or other market sectors to ship the same types of good shipped on pallets containing decaBDE"), there is a functionally equivalent alternative to plastic pallets containing decaBDE.

The PECO and CHEP wood pallets are used currently by the grocery industry or other market sectors to ship the same types of goods that are shipped on pallets containing decaBDE. A third pallet, the new CHEP plastic pallet, which just went into production at the beginning of December 2010, has been designed for use in that market. It is too early to say whether or not it will be used by companies using open pool services to ship the same types of goods, but CHEP's market position as the largest open pool pallet company certainly makes this plausible. As a plastic pallet with a non-halogenated flame retardant, it meets the goal of bringing a plastic pallet with a safer alternative flame retardant into the market. It will be some time before the extent of its potential role in the market will become clear. That will depend both on the attractiveness of the pallet in the market for groceries and other consumer goods commonly shipped on open-pool pallets, and on the extent to which CHEP promotes its use as an alternative to wood pallets as well as to the decaBDE plastic pallet. But the production of a plastic pallet with a non-halogenated flame retardant by the largest company in the open-pool pallet market seems to meet the intent of this criterion.

Structure of This Assessment

Assessments of safer alternatives to the use of toxic chemicals in products often focus primarily on the assessment of available chemical substitutes for the function served by the chemical to be replaced. This is both valuable and extremely important, and in many cases may be the only route to a solution. The use of the Green Screen for this report provided just such an assessment of alternative chemicals that could be used as flame retardants. (See Chapter VI for a summary of other chemical assessment tools.)

But Maine DEP also designed this study to assess the safer, non-chemical alternatives that might be developed through a focus on the structure and operations of the industry. This is not always incorporated as a systematic component of the alternatives assessment. In particular, this study looked at fire protection systems and management methods that might provide alternatives. While, in the short term, the stock of older and less protected warehouses makes a solution based entirely on these factors insufficient, the design helped to broaden the perspective of the study to include ways in which environmental health and fire protection goals could converge in future planning.

Introduction

This Alternatives Assessment is a study of safer alternatives to decabromodiphenyl ether (decaBDE) as a flame retardant for plastic shipping pallets. The assessment evaluates the availability of other flame retardants, their potential effectiveness in making a flame retardant plastic pallet, some cost constraints that could affect their development or adoption, and their potential human health and environmental impacts compared to decaBDE. The assessment also investigates the potential to reduce the need for flame retardants in plastic pallets through adoption of more stringent fire protection and management methods by distribution centers and warehouses handling commodities such as groceries, beverages, consumer electronics and other rapid-turnover consumer commodities.

The central question Maine's Department of Environmental Protection (DEP) has set for this study is to determine if there are any functionally equivalent alternatives to the continued use of plastic pallets with decaBDE. Answering this question requires an overview of the services plastic and non-plastic pallets currently provide in the shipping market, the logistical organization of these services, and the current or potential availability of safer, alternative non-halogenated flame retardants that could replace decaBDE in plastic pallets. As part of this assessment, the study also explores some of the complexities and costs of developing a flame retardant plastic pallet based on non-halogenated flame retardants.

DecaBDE is an extensively used fire retardant found in a variety of plastic, electronic, textile, upholstery and building products. It is one of a class of brominated flame retardant (BFR) chemicals, the polybrominated diphenyl ethers (PBDEs), and one of three commercial formulations that served until a few years ago as effective and inexpensive flame retardants. There is increasing evidence of decaBDE's widespread environmental persistence, presence in breast milk and children's blood, and potential liver, thyroid, and neurodevelopmental toxicity, raising concerns about its human health and environmental effects. Maine and other government agencies have acted to reduce use of and exposure to decaBDE, as well as other PBDE compounds, by enacting laws that either prohibit or restrict its use.[11]

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[11] Maine Department of Environmental Protection and Maine Center for Disease Control reported to Maine's legislature in January 2007 that the decaBDE flame retardant "is a persistent, bioaccumulative and potentially toxic chemical…. The slow release of decaBDE from [consumer] products has led to widespread environmental contamination. Levels in human tissue, human breast milk and the food we eat are cause for concern." *Brominated Flame Retardants: Third Annual Report to the Maine Legislature*, January 2007, http://www.maine.gov/dep/rwm/publications/legislativereports/pdf/finalrptjan07.pdf.

DecaBDE is a synthetic chemical that does not occur naturally in the environment. It is differentiated from other members of the chemical family of polybrominated diphenyl ethers (PBDEs) by having ten bromine atoms. Other members of the PBDE family with fewer bromine atoms, such as pentaBDE with five bromine atoms, are generally considered to have greater acute and chronic effects than decaBDE. Nonetheless, decaBDE itself is on the European Union's (EU) priority list of endocrine disruptors, and has been evaluated as having very high aquatic toxicity and persistence in the environment. Its major targets in humans are the liver, kidneys, spleen and fat.[12] In addition, there is evidence that decaBDE decomposes in the environment to the more toxic molecules containing fewer bromine atoms.[13] Further, recent studies indicate that decaBDE is bioaccumulating in humans, suggesting the potential for increased health risks from continued exposure.[14]

In 2004, Maine's legislature banned sale or distribution of products containing the penta or octa PBDE congeners[15] and declared its intention to reduce risks to the public from exposure to decaBDE, "by implementing risk management measures or by prohibiting the sale of products containing … the deca mixture … if a safer, nationally available alternative is identified."[16] In 2007, Maine passed legislation banning sales or distribution of televisions and computers with housings containing decaBDE. At that time, most of the worldwide production of decaBDE was thought to be used in the plastic casings of TVs.[17] Subsequently, at the end of 2009, the United States Environmental Protection Agency (USEPA) reached an agreement with the two U.S. manufacturers and the largest importer of decaBDE to eliminate its use in consumer products by the end of 2012 and to stop use entirely by the end of 2013.[18]

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[12] See Appendix IX, Green Screen for decaBDE.

[13] Alcock RE, Busby J., "Risk migration and scientific advance: the case of flame-retardant compounds". *Risk Anal.* **26** (2: 369–81), April 2006. doi:10.1111/j.1539-6924.2006.00739.x. PMID 16573627

[14] Thuresson, K., Höglund, P., Hagmar, L., Sjödin, A., Bergman, Å., and Jakobsson, K. (2006). Apparent half-lives of hepta- to decabrominated diphenyl ethers in human serum as determined in occupationally exposed workers. Environ. Health Perspect. 114:176-181.

[15] Structurally similar chemicals with differing numbers of bromine atoms – penta (5 bromine atoms), octa (8), deca (10).

[16] "An Act To Reduce Contamination of Breast Milk and the Environment from the Release of Brominated Chemicals in Consumer Products," 2003 Laws of Maine, Chapter 629, http://www.legislature.maine.gov/ros/lom/LOM121st/14Pub601-650/Pub601-650-33.htm. Also in 2004, the European Union banned the use of penta and octa PBDEs, and EPA reached an agreement with the sole US manufacturer to cease production by the end of that year.

[17] The Maine law also banned the sale of mattresses, mattress pads and residential upholstered furniture containing decaBDE in anticipation of the adoption of federal flame retardancy standards for those products. DecaBDE is not known to be used in these products currently.

[18] "An Act to Protect Pregnant Women and Children from Toxic Chemicals Released into the Home," Maine Public Law, Chapter 2H.P. 1167 – L.D. 1658, effective September 20, 2007. http://www.mainelegislature.org/legis/bills/bills_123rd/chapters/PUBLIC296.asp. US EPA,

Legislative Background for DecaBDE Phaseout in Plastic Shipping Pallets

Maine's 2007 law was intended to eliminate the major residential use of decaBDE in the state by phasing out its use in TV housings. The use of decaBDE in plastic shipping pallets is recent and was not covered by the legislation. In 2010, the Maine Legislature addressed this new decaBDE usage in "An Act to Clarify Maine's Phaseout of Polybrominated Diphenyl Ethers," (the Act).[19]

The new law stipulates:

- Effective January 1, 2012, no one can, "manufacture, sell or offer for sale or distribute for sale or use in the State a shipping pallet containing the deca mixture of polybrominated diphenyl ethers…."
- Effective immediately, no one can sell, distribute or use a product made from recycled shipping pallets containing decaBDE – with the sole exception of new shipping pallets made from recycled shipping pallets containing decaBDE.[20]

The law includes some exemptions, both temporary and permanent, to the sales ban.

- A company may seek a temporary exemption, valid only until January 1, 2013, based on one of the following four findings:[21]
    - No "safer alternative" exists that meets the above (subsection 14) criteria.
    - A pallet with a proposed safer alternative fails to meet fire safety or relevant performance requirements.
    - Additional time is needed to test a pallet with a safer alternative against fire safety or performance requirements.
    - Additional time is needed to modify the manufacturing process to produce a pallet with a "safer alternative."
- A company may continue to distribute or use shipping pallets containing decaBDE after January 1, 2013, if manufactured before January 1, 2012.[22]

"Polybrominated Diphenyl Ethers," http://www.epa.gov/opptintr/pbde/; http://www.buildinggreen.com/auth/article.cfm/2010/2/1/Industry-Agrees-to-Phase-Out-DecaBDE-Flame-Retardant/; letter from Albemarle Corporation to Lisa Jackson, December 15, 2009, www.epa.gov/oppt/existingchemicals/pubs/actionplans/Albemarle.DecaBDE.pdf.

[19] 2009 Laws of Maine, Chapter 610 [herein PL2009, c.610], "An Act to Clarify Maine's Phaseout of Polybrominated Diphenyl Ethers."
http://www.mainelegislature.org/legis/statutes/38/title38sec1609.html &
http://www.legislature.maine.gov/legis/bills/bills_124th/chapters/PUBLIC610.asp

[20] See PL 2009, c. 610, § 2 enacting 38 MRSA §1609, sub-§5-A
http://www.legislature.maine.gov/legis/bills/bills_124th/chapters/PUBLIC610.asp

[21] 38 Maine Revised Statutes § 1609, sub-§ 5-B.
http://www.legislature.maine.gov/legis/bills/bills_124th/chapters/PUBLIC610.asp

- A company may manufacture, sell, distribute or use shipping pallets after January 1, 2013 made from recycled shipping pallets containing deca.[23]

Finding "Safer Alternatives"

A central feature of Maine's law on decaBDE is the requirement to find a "safer alternative" to replace decaBDE's role as a flame retardant. The legislation stresses both the practical need to find an alternative to decaBDE that is effective and commercially available, and to ensure that companies do not substitute alternative flame retardants with other serious toxicity problems.[24]

For plastic shipping pallets, the 2010 law requires the replacement of decaBDE with a "safer alternative" (whether chemical, product or management strategy) that meets the following criteria:[25]

- Reduces the "potential for harm to human health or the environment…." Any potential chemical alternative (or its breakdown products) must not be defined by USEPA as a persistent, bioaccumulative and toxic [PBT] chemical, and cannot be a brominated or chlorinated flame retardant.[26]
- "Serves a functionally equivalent purpose" for fire safety and performance.
- "Is commercially available on a national basis."
- "Is not cost prohibitive."

Purpose of Alternatives Assessment Study for Use of DecaBDE in Plastic Shipping Pallets

Section 9 of the Act calls for an alternatives assessment study by the Department of Environmental Protection (DEP) to evaluate the availability of measures and alternatives for shifting from decaBDE to safer alternatives "as soon as practicable."[27] The study must consider fire safety standards, tests and approvals as well as relevant performance specifications. DEP commissioned this study to assess two alternatives:

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[22] 38 MRSA section 1609, subsection 11 (A-1).

[23] 38 MRSA section 1609, subsection 5-A (B).

[24] In 2007, the Maine Department of Environmental Protection and Maine Center for Disease Control reported to the legislature that there were alternative flame retardants to replace decaBDE in the consumer products in which decaBDE was commonly used. *Brominated Flame Retardants: Third Annual Report to the Maine Legislature,* January 2007, http://www.maine.gov/dep/rwm/publications/legislativereports/pdf/finalrptjan07.pdf.

[25] 38 MRSA Section 1609, subsection 14.

[26] A decaBDE replacement can include 0.1% of PBTs or brominated or chlorinated flame retardants, or 0.2% of a halogenated organic chemical containing fluorine. 38 MRSA Section 1609, subsection 14(B).

[27] Section 9, "An Act to Clarify Maine's Phaseout of Polybrominated Diphenyl Ethers."

- The availability of safer nonhalogenated alternative chemical flame retardants for plastic shipping pallets; and
- The potential for using best management practices in lieu of flame retardants to meet fire safety requirements.

With respect to the first of these alternatives, the goal of this report is to determine pallets with safer nonhalogenated alternative flame retardants are functionally equivalent to pallets containing decaBDE. Functional equivalence will be evaluated according to the following criteria established by DEP:

> *"For the purpose of the study, a pallet will be considered functionally equivalent if:*
>
> - *The pallet meets the Grocery Industry Pallet Performance Specifications as set forth on page 11 of the Recommendations on the Grocery Industry Pallet System, Cleveland Consulting Associates, 1992 or is capable of being manufactured to meet those standards; or*
> - *The pallet currently is used by the grocery industry or other market sectors to ship the same types of good shipped on pallets containing decaBDE."*[28]

Preparation of This Report

Maine's Department of Environmental Protection commissioned Pure Strategies, Inc.[29], a Massachusetts consulting firm that works with states, public interest groups and businesses on the sustainability and use of environmentally safer materials, to develop a report assessing whether functionally equivalent safer alternatives are available. Two firms with specialized expertise have supported this work and provided sections of the report. Flame Retardants Associates, Inc.[30], a company specializing in the field of specialty polymer additives, particularly flame retardants and smoke suppressants, wrote sections of the report and provided information on the range of available non-halogenated alternative flame retardants for decaBDE and the technical and economic challenges of their use in pallets. ToxServices[31], a toxicology risk assessment consulting firm, prepared the Green Screens of the potential alternative flame retardants identified during this study and wrote the section of the report summarizing those results. ToxServices had previously supported the development of Clean Production Action's Green Screen for the assessment of chemicals' environmental and human health impacts. The sections of the report these two firms prepared are identified at the beginning of each section.

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[28] DEP, "Specifications of Work to Be Performed" (as amended 10-13-10).

[29] http://www.purestrategies.com

[30] http://www.flameretardantsconsultants.com/

[31] http://www.toxservices.com/

Chapter I: Plastic Shipping Pallets: Markets & Uses

Plastic Pallets as a Part of the Entire Shipping Pallets Market

Shipping pallets come in a wide variety of shapes and sizes, and are used both for storing and for shipping a vast array of consumer goods and industrial products throughout the United States each day. While estimates vary, most sources figure that approximately three billion pallets are in use in the U.S. Pallets are made of a variety of materials: wood, plastic, aluminum, steel, corrugated paperboard, and composite wood. The dominant pallet material is wood, with well over two billion of these in use, accounting for about 80% of the annual demand for new or repaired pallets. While much smaller in terms of the total pallet market, plastic is the second largest, and fastest growing, pallet material. Over 900 million plastic pallets are in use, and demand for plastic pallets is projected to increase by more than double the total annual pallet growth rate (2.4% vs. 1%) in the near future. A 2008 study[32] estimated that by 2012 the total annual market for pallets could be 1.5 billion, of which 130 million would be plastic. Other pallet materials will play smaller or specialty roles.

Figure 1.1. Pallets made from wood, plastic, and metal

Wood Pallets Plastic Pallet Metal Pallet

As Table 1.1 illustrates, pallet size varies by market sector, depending on factors such as strength, weight, cost, durability, and the shipping or storage requirements of the

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[32] "Pallets: One Size Fits Nobody," Pacific Design & Manufacturing, September 1, 2008. http://mhlnews.com/transport-packaging/mhm_imp_6438/; "Plastic Pallets Gain Ground in an Eco-Conscious World," September 1, 2008. http://www.thefreelibrary.com/Plastic+pallets+gain+ground+in+an+eco-conscious+world-a0185165596; The Freedonia Group, *Industry Study: Pallets*, June 2008. Robert Bush and Philip Aranon, "Updated Pallet and Container Industry Production and Recycling Research," USDA-Forest Service, SRS 04-CA-11330142-205, October 2008.

specific sector.[33] The most common type of pallet is the 48x40 'grocery' pallet (for rapid-turnover consumer products such as foods, laundry detergents, paper towels and many others), constituting about 30% of the total pallet market. This is the category where plastic pallets play their largest role, though wood pallets still predominate.

For assessing alternatives to using plastic pallets with decaBDE flame retardants, the uses and requirements for the 48x40 plastic pallet are the most important to consider. This is the pallet most frequently made with flame retardants (for reasons that will be discussed below), though flame retardant plastic pallets are still a minority of these pallets.

Table 1.1: Sizes and Uses of Pallets

Dimensions, inches (W × L)	**Production Rank**	**Industries Using**
48 × 40	1	Grocery, common in many other industries
42 × 42	2	Telecommunications, Paint
48 × 48	3	Drums
40 × 48	4	Department of Defense, Cement
48 × 42	5	Chemical, Beverage
40 × 40	6	Dairy
48 × 45	7	Automotive
44 × 44	8	Drums, Chemical
36 × 36	9	Beverage
48 × 36	10	Beverage, Shingles, Packaged Paper

Performance Standards for the 'Grocery' Pallet

In the early 1990s, the Grocery Manufacturers Association (GMA) published specifications designed to bring greater uniformity to the design and attributes of the 48x40 grocery pallet in order to ensure that pallets used for shipping grocery products would meet basic standards.[34] These standards focused both on ensuring that pallets would not create any risks for the transported foods and on facilitating the most efficient movement of goods between different companies.

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[33] Table from: Clarke, John, "Pallets 101: Industry Overview and Wood, Plastic, Paper & Metal Options," www.ista.org/forms/Pallets_101-Clarke_2004.pdf.

[34] See Grocery Industry Pallet Performance Specifications from "Recommendations on the Grocery Industry Pallet System" in Appendix II.

The GMA standards cover a number of areas:

- *Fire protection*: GMA pallets “must meet or exceed current pallet resistance to fire.”
- *Size and structure*: Pallets must be 48x40 inches; no more than 6 inches in height; have minimum 85% coverage on the (non-skid) top surface of the pallet; 60% coverage on the bottom surface; have ‘4-way entry’ (openings that allow forklifts and other equipment to lift the pallet from any direction); and meet other technical criteria to facilitate consistency with pallet management equipment.

Figure 1.2: Four-Way Entry Pallet

- *Weight:* Less than 50 pounds.
- *Sanitation:* Made of material that does not contaminate the product it carries.
- *Durability:* Capable of ‘multiple cycles.’
- *Strength:* Capable of holding 2800-pound loads both in racks (which provide support only for the edges of the pallets) and, on a flat surface, in stacks five loads high (each fully loaded with 2800 pounds).[35]

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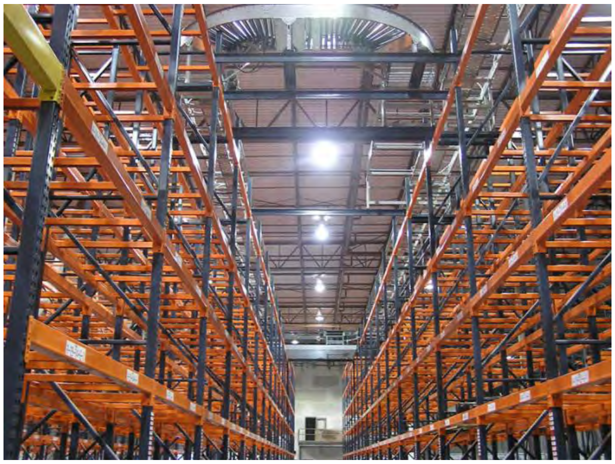
[35] This latter standard has been superseded by an industry standard of 30,000 pounds.

Figure 1.3: Empty Racks Used for Pallet Storage



- *Recyclable:* Preferably made from recycled materials.
- *Repairable:* At reasonable cost.
- *Moisture and weather resistant.*

The GMA standard, while not formalized as a consensus standard through an organization such as the American National Standards Institute (ANSI), is widely referenced as a series of goals pallets should meet, especially pallets used for shipments between different companies (e.g., from a Kellogg's or Kraft manufacturing site to a grocery warehouse). Some of the criteria are clearly critical (e.g., 48x40, 4-way entry). But even for inter-company 'grocery' shipments there are some variances. For example, the standard requirement for the strength of stacked pallets is generally 30,000 pounds (rather than the 14,000 pound requirement for holding five 2800-pound loads), and the wood pallets that dominate in such pooled inter-company transfers generally weigh well over 50 pounds. In addition, many pallets are designed to meet more limited, specific purposes. But the GMA standards, and more recent technical performance standards, play an important role in efforts to develop plastic pallets with non-decaBDE flame retardants, since the flame retardants can have significant impacts on these other performance needs (see Chapter 3).

Some Different Types of Plastic 48x40 Pallets

Within the category of 48x40 plastic pallets used for shipping and storing food and consumer products, pallet users can choose from a variety of options depending on specific needs. The following are a few examples of plastic pallets serving different functions.

- *Rackable/stackable pallets:* These pallets are used for shipping products from manufacturers/producers to end-users, and for storing products on racks or in stacks in a warehouse or distribution center. While individual attributes (such as specific load-bearing capacity or whether the pallet is fire retardant) can vary depending on whether these pallets are used in a 'captive' system (e.g., controlled by a single company) or for rental/leasing use involving different companies, these pallets are designed for carrying or storing heavy leads. If used for shipping/storing products outside a closed-loop or captive system, these pallets should be capable of holding 2800-pounds when suspended between two beams of a warehouse storage rack (rackable) and up to a 30,000-pound static load supported by a solid platform (stackable).

Rackable/Stackable Plastic Pallet

Manufacturer: Schoeller Arca

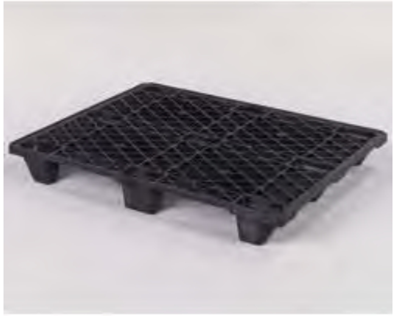
- *Nestable pallets*: Light weight pallets (e.g., 20-30 lbs.) are generally used for moving products within a single warehouse or distribution center, between facilities within a single organization, or in a closed-loop between cooperating businesses, such as between a warehouse and the retail outlets of a single company. When not in use these pallets fit together (nest) to minimize storage space and shipping space. Because of their light weight, they can be handled more easily at end-user stores than any of the stronger rackable or stackable pallets. Correspondingly, they do not have the necessary load-bearing capacity to be used for such storage. They are not generally made with flame retardants. These pallets tend to be in fairly continuous use, but their nesting ability substantially reduces the stack heights required for temporary storage – an important benefit for compliance with fire prevention regulations (see below in Chapter II).

Nestable Plastic Pallet

Manufactured by Rehrig-Pacific

- *One-way/international pallets:* When sending products overseas by air, shippers may have little expectation of seeing the pallets returned. Shippers also want to avoid paying high air freight costs for heavy shipping pallets. One option is to use very light pallets (12-19 pounds) specially designed for international air travel, and possibly, one-way use. These pallets have limited load capacity, and could not be used for racking or stacking products.

International/One-Way Plastic Pallet



Manufactured by CABKA

What Criteria Drive Pallet Selection?

There is a wide range of options available to the logistics, operations and warehouse managers who make purchasing decisions on pallets, both generally and for the 48x40 'grocery' pallets that principally concern us with respect to fire prevention and flame retardants. A recent survey of such managers by Modern Materials Handling (MMH) indicates that individual facilities may make different selections for different purposes. For example, the survey results demonstrated a significant percentage of mixed purchasing of wood, plastic or other types of pallets based on diverse needs within single operations (Table 1.2).[36]

Table 1.2: Purchasing Patterns

Pallet Material	**% Purchasing Pallets Made of Each Material** (may buy multiple types)
Wood	92%
Plastic	33%
Engineered wood (e.g., plywood)	15%
Cardboard/corrugated	10%
Metal	6%
Other	3%

The MMH survey also asked respondents what factors were most influential for them when they were making decisions to buy either plastic or wood pallets. Not surprisingly, cost is important when choosing either plastic or wood.

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[36] "Pallet Usage and Trending Study," *Modern Materials Handling*, October 28, 2010.

Table 1.3: Survey Respondents' Reasons for Selecting Plastic or Wood Pallets[37]

Attribute "very important"	When Selecting Plastic Pallets - %	When Selecting Wood Pallets - %
Purchase price	61	70
Durability	58	49
Strength	57	56
Cost per use	55	52
Reusability	53	34
Availability	42	54
Easy to clean	38	20
Recyclability	32	25
Weight	31	21
Design versatility	26	16
Ease of disposal	24	17
Fire rating	19	11
Ease of repair	15	19

Not only is cost the factor most frequently cited for selecting both plastic and wood pallets, but some of the other factors, such as durability and reusability, are directly or indirectly related to cost as well. If a manufacturer is sending pallets it purchases overseas, or domestically to locations from which it is unlikely to recover the pallets, then the lowest cost pallet that will hold up in transit is important (or, alternatively, with large volumes, pooling may be the best way to reduce costs). If pallets will be in a captive system where they are used only between different facilities from the same company (e.g., between Hannaford's warehouse and Hannaford stores), then higher-priced durable pallets may be the lower-cost, long-term option. There are also some differences in reasons for selection of wood or plastic, such as a greater emphasis on availability in selecting wood or on weight (for fuel efficiency or reduced worker injuries) in selecting plastic.

Buying or Renting/Leasing Pallets

In addition to deciding whether to use pallets of wood, plastic or other materials, companies also can choose either to buy pallets directly for their own use, or to rent or lease pallets that are managed and repaired by companies that specialize in pallet

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[37] Respondents were not limited to a single response. In many cases a facility or company might buy both plastic and wood pallets for different purposes. The survey also has an "important" category, but the same 6 attributes remain highest in importance when 'very important' and 'important' responses are added. "Pallet Usage and Trending Study," *Modern Materials Handling*, October 28, 2010.

management. A warehouse or logistics manager who decides to out-source pallet management can lease pallets with delivery and repair contracts to meet its needs, or can turn to companies that provide 'open-pooling' pallet management/rental systems (see below).[38]

Whether a company chooses to buy pallets or to participate in a pallet rental or open-pooling system depends to a significant extent on how the pallets will be used. For example, a company using pallets only for internal warehouse storage and movement, or for moving goods between its own facilities is more likely to purchase and manage the pallets it uses, while a company sending goods on a routine basis to a variety of buyers all over the country stands to benefit more from a rental service.

Overall, companies buy and self-manage far more pallets than they rent. Only a third of managers responding to the MMH survey reported making use of pallet retrieval, recovery or rental systems, and slightly more than 10% specifically reported using pallet rental services. In the universe of 48x40 grocery pallets, the three major, open-pooling rental companies manage approximately 90 million pallets – approximately 10% of the total number of 48x40 pallets in use.[39]

Open-Pool Pallet Leasing

Open-pooling of pallets is more important – both commercially and for the search for alternatives to the use of decaBDE – than the numbers above suggest.

- Open-pool 'grocery' pallets move relatively rapidly in commerce, as that is how the open-pooling companies make their money.
- Many of the largest companies in high-turnover, consumer products – from manufacturers to retailers – use open pooling services.
- Open-pooling of pallets is growing.
- While a relatively small percentage of plastic pallets sold directly to users are made with flame retardants, virtually all plastic pallets in open-pooling systems are made with flame retardants.

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[38] There are also 'closed loop' pallet systems where one or more companies move products on their own pallets from manufacturing or distribution centers to stores or regional warehouses, and then return those pallets for reuse. Smaller companies may share pallet purchasing, management and/or repair systems for increased efficiency such as for sharing truckloads of goods.

[39] According to data reported by MMH, the three largest open-pooling companies use between 80-90 million pallets, while the total universe of 48x40 pallets (approximately 30% of 3 billion total pallets) is about 900 million. See articles on CHEP, iGPS and PECO in the October 6, 2010 issue of MMH magazine: http://www.mmh.com/article/pallets_and_containers_the_plastic_pool_alternative/, http://www.mmh.com/article/pallets_and_containers_a_chep_off_the_old_block/, http://www.mmh.com/article/pallets_pallet_pooling_for_the_other_guys/.

While a small proportion of the total shipping pallet universe, open pooling of pallets plays a major role in shipping consumer goods from manufacturers or food producers to distribution centers and warehouses for wholesalers and retailers. Large national companies such as Kellogg's, SC Johnson, Kraft Foods Inc., and Pepsi, use open-pooled pallet systems to distribute their products to hundreds of retail distribution centers and grocery warehouses around the country.

There are three major open-pooled pallet management companies in the U.S. that provide this service – CHEP, Intelligent Global Pooling Systems (iGPS), and PECO Pallet (PECO) [40]. CHEP is the goliath of the business, with approximately 65 million pallets in use. Originally it was the only major player, but both iGPS (approximately 10 million pallets) and PECO (5 million pallets) have emerged during the last decade. CHEP and PECO both provide wood pallets (though CHEP has a very small number of plastic pallets, and just began manufacture of a new plastic pallet at the beginning of December 2010). IGPS has broken into the market with a plastic pallet, clearly differentiating itself from CHEP. All of these pallets are 48x40 pallets used for groceries and other rapid turnover consumer goods.

How open pooling works

Figures 1.4 and 1.5 below provide a schematic overview of how open pooling systems work. Figure 1.4 illustrates the basic process:

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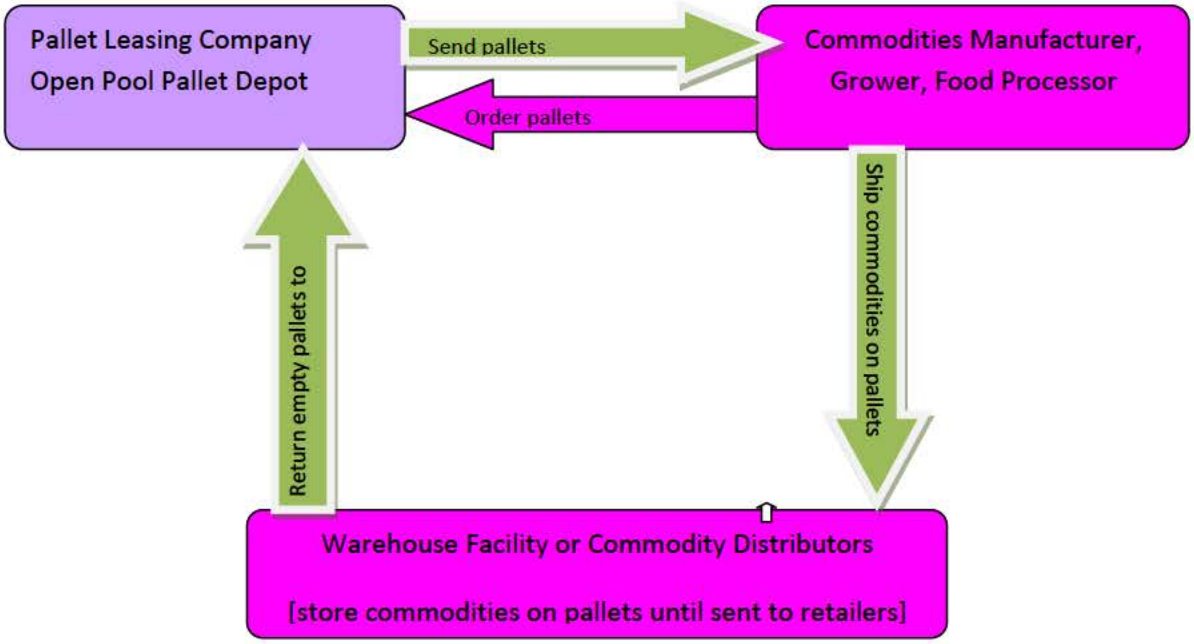
[40] See articles on CHEP, iGPS and PECO in October 6, 2010 issue of MMH: http://www.mmh.com/article/pallets_and_containers_the_plastic_pool_alternative/, http://www.mmh.com/article/pallets_and_containers_a_chep_off_the_old_block/, http://www.mmh.com/article/pallets_pallet_pooling_for_the_other_guys/.

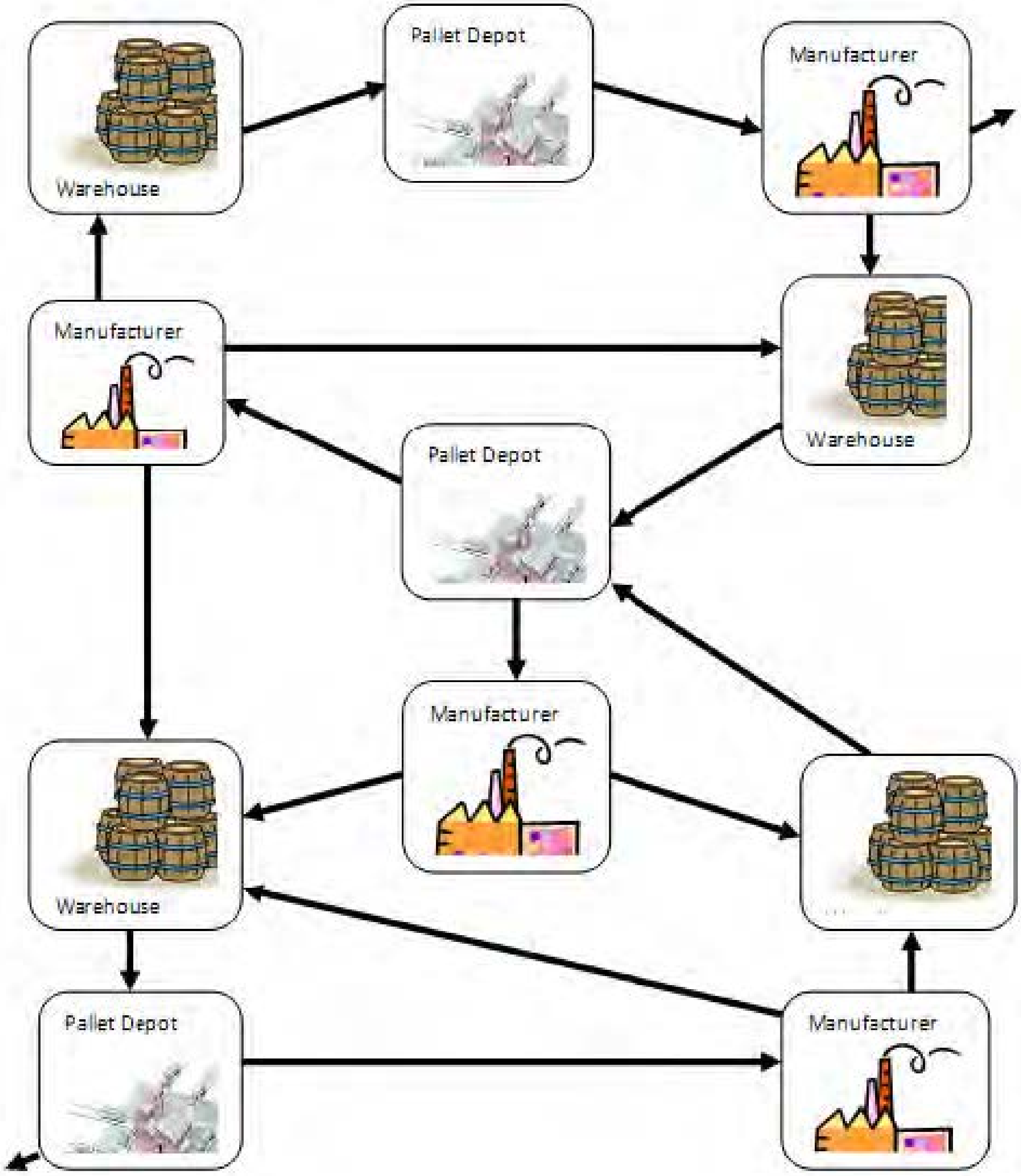
Figure 1.4: Schematic of Open-Pool Pallet Leasing



- A company with an agreement with an open pooling company (CHEP, iGPS or PECO) sends an order for a truckload or more of pallets for one of its manufacturing/production centers.
- The open-pooling company sends the pallets from one of its pallet depots to the manufacturer.
- The manufacturer loads the pallets and sends them to a variety of different warehouses or customer distribution centers around the country.
- The pallets may be unloaded immediately or used for some time for storage of commodities until ready for redistribution to retail stores, restaurants, hospitals, etc.
- Once unloaded, the pallets are stored at the warehouse until a truckload of pallets is ready for collection by the pooling company which returns them to a nearby pallet depot.
- At the depot, pallets will be cleaned, repaired, recycled or replaced as necessary.
- The process is repeated.

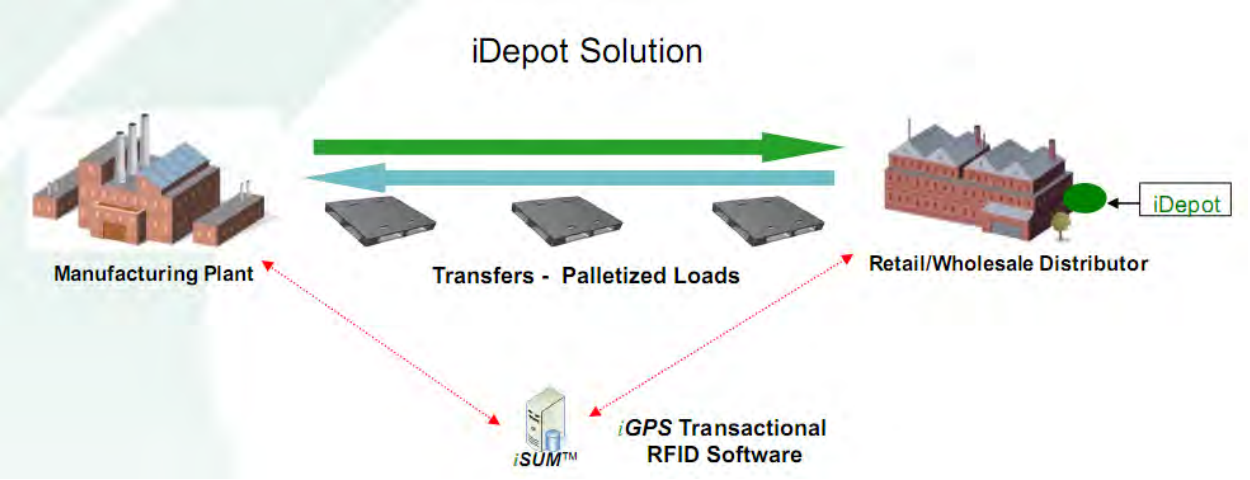
Figure 1.5 illustrates that the pooling system is ‘open,’ as the same pallet may go to a different user each time. The pallet moves from depot to manufacturer to warehouse (or, occasionally, retail store) to another depot, and then another manufacturer, another warehouse, etc., as it is leased to different users for shipping their products.

Figure 1.5: Movements of Pallets between Various Users in Open Pooling



The key to profitability for CHEP, iGPS and PECO is for their pallets be in constant use, and to ensure that pallets are effectively tracked so that as few pallets as possible are lost. While all three companies have systems to keep track of their pallets, iGPS uses a radio frequency identification (RFID) tracking system that iGPS believes makes it possible to cut a step out of the pallet cycle. IGPS has agreements with some warehouses that receive merchandise on iGPS pallets to check and clean the pallets at the warehouses so they can be sent directly to the next user without going back to an iGPS pallet depot (Figure 1.6).[41]

Figure 1.6: Open Pooling without Returning Pallet to Depot



How Do Facilities/Companies Use Pallets?

An important factor in deciding whether to purchase pallets or use a pallet rental service is the anticipated use of the pallets. As the following information from the MMH survey demonstrates,[42] most operations have multiple uses, and may use different pallets for different purposes.

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[41] Information from Lew Taffer, iGPS, October 4, 2010. Figure 1.6 provided by Lew Taffer.

[42] "Pallet Usage and Trending Study," *Modern Materials Handling*, October 28, 2010.

Table 1.4: How Companies/Facilities Using Pallets

(Companies may use pallets for more than one purpose)

How Pallets are Used in Operations	%
Within a facility	76
One-way between trading partners	65
Between company facilities	55
When exporting	38
Closed-loop between trading partners	23
Other	5

There are many variations in how pallets may be used, from limited internal movement of materials within a manufacturing center to a variety of movements between facilities of the same or different companies. The following examples illustrate some of the options:

- *Hannaford warehouse in South Portland, Maine*: The Hannaford warehouse receives a vast array of groceries, beverages, cleaners, and other consumer products from major companies and distributors, and re-distributes them to Hannaford stores throughout New England. Inbound products come in on both wood (predominantly) and plastic pallets, including pallets from the three major open-pooling companies, and some additional white wood pallets and occasionally other types of pallets. The goods arriving on the pooled pallets or those of higher quality white wood are stored on those pallets on racks until ready for re-distribution to stores. These pallets weigh from slightly less than 50 pounds for plastic up to 65 or70 pounds for wood. The goods and their pallets are moved by forklift or mechanized systems. After the products are removed from the pallets for shipment to individual Hannaford stores, the empty pallets are stored until a truckload of pallets is ready for pickup by the appropriate company.

  To send products to individual Hannaford stores, an appropriate mix of products is placed on light-weight (less than 30-pound) “nestable” plastic pallets that, while not strong enough to use for storing products in racks, are easier for store personnel to handle. Once empty, these nestable pallets are returned from Hannaford stores to the Hannaford warehouse.[43]

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[43] Personal communication from Al Hussey, Manager, Hannaford warehouse, South Portland, Maine, September 13, 2010.

- *Sysco of New England, warehouse in Westbrook, Maine:* Inbound freight for the Sysco warehouse usually arrives on wood (95% on CHEP pallets and the rest on inexpensive white wood pallets) and is stored in the warehouse largely on the CHEP pallets. To send products from the warehouse to customers, Sysco moves the goods onto lightweight nestable plastic pallets. None of these contain flame retardants. The warehouse buys the plastic pallets from Rehrig Pacific Company at a cost ranging from $28-33, depending on the crude oil price.

  The plastic pallets are a substantial cost to the warehouse, but the warehouse chose them for two reasons. The first concerns sanitation; the plastic pallets can be washed, whereas wood can harbor spills and bacteria, and is frowned on by food safety auditors. The second reason is convenience. Once pallets going to stores are unloaded, empty pallets can be stored on the truck as it moves to the next store and plastic pallets can be strapped to the sides of trucks to make easier unloading at subsequent stores. Wood pallets are too heavy for this and must be left on the truck floor where they may be in the way.

  For the most part, the plastic pallets go to customers, are unloaded and then returned. But the warehouse has had problems with high attrition rates (eight years ago, as high as 30%/year), largely due to drivers leaving pallets with customers. Driver training, stressing the expense to the company, has reduced the loss ratio to as little as 5%/year. Because of the cost factor, Sysco now ships to stores on Maine's coastal islands on cheap wood pallets, because the pallets sent there rarely come back.[44]

- *Sunny Delight Beverages Co. (Sunny Delight):* Sunny Delight primarily uses open pooled pallets for sending products to its customers, and recently shifted to iGPS plastic pallets. Two major factors led to Sunny Delight's decision to switch from wood pallets to plastic pallets – both related to cost. As beverage products are relatively heavy, lightening the total load by reducing pallet weight represents a significant potential savings in fuel use. Second, the use of RFID tracking of the iGPS pallets allows integrated control of data on inventory and deliveries with automated reconciliation on pallet use. This system could potentially allow fully automated warehouse operations – with possible major long-term cost savings. While Sunny Delight had heard concerns that the presence of decaBDE could impair their products, the industrial hygiene firm

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[44] Personal communication from David Thomason, VP, Operations, Sysco of Northern New England, October 26, 2010.

they hired to do assessments found no air or dust issues. While it uses pooled plastic pallets wherever possible, Sunny Delight uses heat-treated wood pallets for deliveries to the Caribbean and Mexico, due to the difficulties of retrieving pallets delivered to locations in those regions.[45]

- *Kellogg's:* Kellogg's primarily uses wood pallets. These include both open pooled pallets (CHEP) for large commercial customers and some white wood for deliveries to smaller customers. The company is working to convert its entire network to pooled pallets. Externally, customers are major drivers in the choice of pallet for deliveries. Internally, Kellogg's has some captive pallets for moving items around in production facilities; mostly these are white wood pallets, though there are a few nestable plastic pallets (for which Kellogg's gets about 32 cycles before sending them in for reforming). For international shipments, Kellogg's uses heat-treated wood pallets to meet international phytosanitary standards.

  While they are generally happy with wood pallets, there have been some issues. One concern was the potential impact of having wood pallets in the production area; Kellogg's doesn't want pieces of wood where food is processed. They solved this by bringing wood pallets to the outskirts of the production area and loading products on the pallets as ready-to-ship products. Another potential consideration has been the weight of the wood pallets. This is not so much an issue for shipping cost, because Kellogg's products are very light. It is more an ergonomics issue for workers. To avoid any adverse effects, Kellogg's uses equipment – such as forklifts and pallet dispensers -- for handling the pallets.[46]

Pooling & Purchase: Separate Markets

As these examples illustrate, the markets for pallet purchasing and pallet pooling are, to a significant degree, distinct. A company's internal (captive) operations involving movement within or between facilities or infrequent or small one-way shipments are far more likely to involve pallet purchases than open pooling. Pallet manufacturers focusing on this market can sell directly to large captive operations, or sell to distributors who market pallets to smaller buyers.

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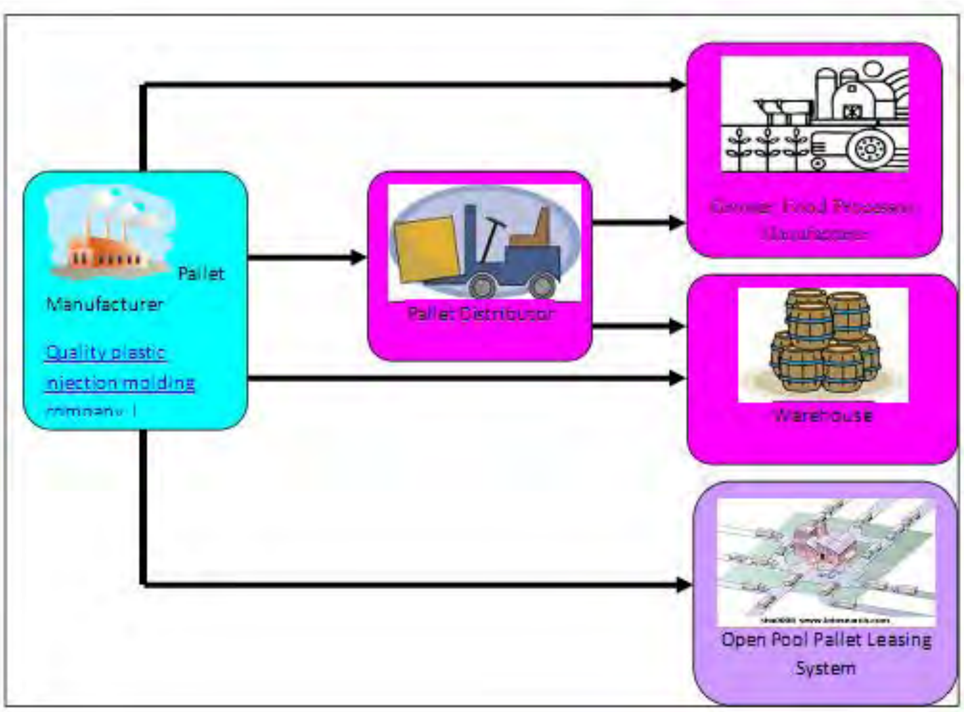
[45] Personal communication from Keith Singleton, Logistics Manager, Sunny Delight, October 29, 2010.

[46] Personal communication from Linda Maupin, Director, Foreign Trade and Distribution Services, Kelloggs, November 16, 2010.

For the hundreds of companies shipping to widely diverse buyers all over the country such as grocery chains and mass merchandising stores, open pooled pallet shipping arrangements are an ideal way to outsource logistical challenges. The differences between these two markets are important for considering the safer alternatives to continued use of decaBDE as a flame retardant in plastic pallets.

Figure 1.7: Markets for Pallets



Plastic Pallet Manufacturers

While plastic pallet manufacturers sell flame retardant pallets directly to end users, flame retardant pallets constitute a relatively small part of the direct sales market for plastic pallets.[47] The largest buyer of flame retardant plastic pallets is the open-pooling pallet company, iGPS. Pallets for iGPS are made by the manufacturer Schoeller Arca

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[47] For example, only approximately 5% of the plastic pallets that Orbis sells are made with flame retardants. Personal communication from Curt Most, Orbis, September 21, 2010.

Systems. A number of other companies make flame retardant pallets for the open market, and a manufacturer has begun making flame retardant pallets for CHEP during the 4th quarter of 2010.[48]

Table 1.5 provides information on major manufacturers of plastic pallets for the U.S. market. Pure Strategies has identified 19 manufacturers and 62 distributors[49] of various types of plastic pallets. Pallet manufacturers are plastic molders. Manufacturing pallets requires investment in large, technically complex and very expensive equipment. Once a mold is fabricated to make a part, the manufacturer must sell a lot of parts to pay for the equipment. So, unlike the market for making wood pallets that involves a large number of small companies as well as major producers, plastic manufacturers must be relatively well-capitalized and technically sophisticated. Table 1.5 identifies: manufacturers; the type of plastic produced (e.g., polypropylene (PP), high density polyethylene (HDPE)); whether or not the manufacturer offers a pallet with flame retardant; available information on the type of flame retardant now in use; and available information on efforts by the manufacturer to develop a pallet using a flame retardant other than decaBDE. As Table 5 shows, only seven manufacturers are currently marketing flame retardant plastic pallets and two companies are distributing flame retardant pallets through the open-pool leasing system.

Table 1.5: Plastic Pallet Manufacturers [50]

Manufacturer	**Pallet Types**	**Polymer Type[51]**	**Flame Retardants Currently in Pallets**	**Status of Development of Pallet with Alternative Flame Retardant**
CABKA North America	Rackable/ Stackable Nestable	Recycled PE & HDPE	None	
Decade Products	Rackable/ Nestable	Recycled HDPE	None	
The Fabri-Form Company	Nestable	HDPE	None	
Greystone Logistics	Rackable/ Stackable Nestable	Recycled plastic	None	
Craemer	Rackable	HDPE	None	

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[48] CHEP has not yet publicly identified this manufacturer.

[49] See Appendix I

[50] Personal communications with Bruce Torrey, iGPS on 8/17/2010; Curt Most, ORBIS on 9/21/2010; Amy Lander, Rehrig Pacific on 9/7/2010; Debbie Bergen, TMF on 9/7/2010. Industry Study 2359 “Pallets” by the Fredonia Group (2008).

[51] Abbreviations: polypropylene (PP); polyethylene (PE); high density polyethylene (HDPE); and polyvinyl chloride (PVC)

Manufacturer	**Pallet Types**	**Polymer Type**[51]	**Flame Retardants Currently in Pallets**	**Status of Development of Pallet with Alternative Flame Retardant**
Mauser Holding GmBH	No data	Recycled PE	None	
Buckhorn (Meyers Industries)	Rackable/ Stackable Nestable	HDPE	None	
ORBIS	Rackable/ Stackable Nestable	PE	Some with flame retardants: DecaBDE Sb_2O_3[52]	Currently developing alternative
PDQ Plastics	Nestable	HDPE	None	
Plastics Research Corporation	Rackable	No information	No information	
Polymer Pallets	No data	PVC	No information	
Polymer Solutions International	Rackable/ Stackable Nestable	HDPE	DecaBDE	
Rehrig Pacific Company	Rackable/ Nestable	PP	Some with flame retardants: Magnesium hydroxide, aluminum trihydroxide, zinc borate	
Rotonics Manufacturing. Inc. (Stratis Pallets)	Rackable/ Nestable	PE	None	
Schoeller Arca Systems	Rackable/ Stackable	HDPE	Sb_2O_3	Currently developing alternative
Shan Industries (Thermodynamics Division)	Rackable/ Nestable	PE	None	
TMF Corporation	Rackable	PE	Some with flame retardants: DecaBDE Sb_2O_3	Currently developing alternative
TriEnda, LLC	Nestable	PE	None	
TranPak	Rackable/ Stackable	No information available	None	
Eco-Tech	Rackable	Recycled PVC plastic	None	
Manufacturer of CHEP pallet	Rackable/ Stackable	PP/ HDPE	Proprietary, phosphorus-based	

A relatively small percentage of plastic pallet manufacturers have produced and marketed flame retardant pallets. For those few, decaBDE has played a major role. But several efforts are now underway to develop alternatives. In addition, as the table makes clear, there is a substantial

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[52] Decabromodiphenyl ether is almost always used in combination with antimony trioxide.

market for plastic pallets without flame retardants. The following chapters will explore the implications of these patterns for finding a safer alternative to use of decaBDE as a flame retardant.

Chapter II: Fire Prevention Concerns and Requirements for Plastic Pallets

The National Fire Protection Association (NFPA) establishes the standard, NFPA 13,[53] that provides the basis for most state and local fire prevention laws and regulations governing warehouse construction and management throughout the country, although state or local requirements may sometimes be more stringent. The NFPA 13 standard includes requirements for management of shipping pallets in warehouses, including requirements that mandate stricter management controls and fire prevention systems for plastic pallets than for wood pallets. For plastic pallets, NFPA 13 provides two options: imposition of more stringent requirements on the warehouse for managing plastic pallets than for managing wood pallets, or use of plastic pallets that have passed tests demonstrating, "a fire hazard that is equal to or less than wood pallets and are listed as such."[54] Use of the flame retardant decaBDE has allowed production of plastic pallets that pass the tests for equivalence to wood.

Finding a safer alternative to the use of decaBDE in plastic pallets requires pursuing one of the following options:

- Implement comprehensive warehouse fire prevention management practices and systems that make it safe to use plastic pallets that are not made with flame retardants
- Develop pallets with alternative safer flame retardants that are effective enough to enable the plastic pallets to be listed as equivalent to wood.[55]

This Chapter reviews the NFPA rules governing these options and their application to warehouse management in Maine.

Pallets & Warehouse Fire Risk

Warehouse fires cause significant property loss every year, as well as creating a risk for loss of life. A NFPA summary of U.S. data for 2003-2006 reports an average of 1,350

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[53] National Fire Protection Association, *NFPA 13: Standard for the Installation of Sprinkler Systems*, 2010 edition. NFPA uses a consensus process approved by the American National Standards Institute (ANSI) to develop its standards.

[54] NFPA 13, Section 5.6.2.6

[55] Another option for meeting the equivalence test includes use of inherently flame-retardant polymers for making a plastic pallet. While a review of this option lies outside the scope defined for this study, the costs of such polymers currently appear prohibitive for application in pallets, with the exception of polyvinyl chloride (PVC). PVC subjected to combustion temperatures decomposes into a variety of highly toxic chemicals including dioxins.

fires in warehouses each year during that period, with annual average losses of $124 million in property and five deaths.[56] While most warehouse fires involve a mix of commodities, packaging, pallets on which the commodities are stored and, in some cases, stacks of pallets not currently in use ("idle" pallets), there are some cases of fires principally involving or caused by pallets – both wood and plastic.

- A National Institute of Standards and Technology (NIST) report in 2000 includes discussion of a warehouse fire in Japan five years earlier in which plastic pallets were stored for use with noncombustible commodities. Although the warehouse had automatic sprinklers that activated after the fire began, the fire overwhelmed the system, lasted 18 hours, and resulted in the deaths of three firemen. The Japanese fire agency concluded that adequate protection against future fires would have to include both an enhanced sprinkler system and a requirement for the use of flame retardants with plastic pallets.[57]
- In September of 2010, a fire in Buffalo, New York at the warehouse of a wood pallet company took hours to control and destroyed the warehouse at a cost exceeding $4 million. "Fire officials say the fire was fueled by wooden and plastic pallets as well as propane tanks stored in the building."[58]

According to an NFPA report, a variety of causes can contribute to starting warehouse fires. This covers direct causes, such as the ignition source that starts the fire, as well as inadequate warehouse management practices. The latter include things as simple as housekeeping to prevent piling up of wood splinters, dust or plastic wrapping. In terms of the direct sources of ignition, NFPA's data for the 2003-2006 period shows the following are the most frequent causes of warehouse fires:[59]

- 14% - Electrical distribution or lighting
- 13% - Intentional
- 11% - Confined trash or rubbish
- 10% - Heating equipment
- 7% - Vehicles

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[56] Marty Ahrens, NFPA, "Structure Fires in Warehouses (Excluding Cold Storage) Fact Sheet," February 2009. www.nfpa.org/assets/files/PDF/WarehouseFactSheet.pdf

[57] "Flammability Test for Flame Retardant Plastic Pallet" by Tokiyoshi Yamada, National Research Institute of Fire and Disaster, and Masahiro Sagara, Japan Pallet Association, in National Institutes of Standards and Technology, U.S. Department of Commerce, *Fifteenth Meeting of the UJNR Panel on Fire Research and Safety*, March 1-7, 2000, Volume 1, p. 89.

[58] "Fire damage at NY pallet company warehouse is $4M," *Palm Beach Post News*, September 10, 2010. http://www.palmbeachpost.com/news/nation/fire-damage-at-ny-pallet-company-warehouse-is-907715.html

[59] Marty Ahrens, NFPA, op.cit.

- 7% - Burners/soldering irons

Once a fire starts, preventing it from leading to catastrophic destruction depends on: the fuel provided by commodities, packaging and pallets; the design and management of storage; and the adequacy of the warehouse's sprinkler control system.

Increased Level of Fire Risks from Plastic Pallets

For shipping pallets, NFPA 13 addresses two sets of potential problems: the risk from fires involving palletized commodities, and the risks from fires involving "idle" pallets. In both cases the standards for plastic pallets are more stringent than those for wood pallets, with the exception noted above for pallets with fire risks equivalent to those for wood. Given both the predominance of wood pallets and the historical emergence of the fire protection rules when alternatives to wood pallets were rare, NFPA 13 treats wood pallets as the base case for the fire protection standards.

Most woods ignite more readily than the plastics, as shown in the table below. The flash-ignition temperature is the temperature at which a spark will cause the materials to catch fire.[60]

Table 2.1

Polymer	**Flash-ignition Temperature (^{O}C)**
Polyethylene	340
Polypropylene	320
Wood (various)	190-260

NFPA treats plastic pallets (or commodities) as a higher risk because, once a fire begins, a fire fueled by plastics becomes more difficult to suppress. The following table shows the comparative heat release factors for some of the plastics and woods used in shipping pallets. The numbers show that the plastics burn at higher temperatures and

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[60] F. Laoutid et al, "New prospects in flame retardant polymer materials: from fundamentals to nanocomposites," *Materials Science and Engineering*, vol. 3, #3, January 2009, Table 1; Tony Café, "Physical Constants for Investigators," T.C. Forensics, Table 2.1, http://www.tcforensic.com.au/docs/article10.html#2.1.2; page updated 2007; Mark Dietenberger, "Ignitability of Materials in Transitional Heating Regimes," FAA, Thermal Analysis of Polymer Flammability (FAA Table 4), DOT/FAA/AR-07. Auto-ignition temperatures are the temperatures at which materials will catch fire spontaneously without a spark. These temperatures are somewhat higher: 350 ˚C for both polypropylene and polyethylene, and 300 ˚C generally for wood, though these temperatures can vary with the type or condition of wood (e.g., the auto-ignition temperature for dry red oak is 482 ˚C). http://www.engineeringtoolbox.com/fuels-ignition-temperatures-d_171.html

thus release more heat than any of the woods. There are differences between the softwoods and hardwoods, and some discrepancies in the figures for heat released by pine wood according to different sources, but all of the values for the woods are substantially lower than those for the plastics.

Table 2.2[61]

Heat Release of Some Plastics/Woods Used in Shipping Pallets

Polymer	ASTM D 2015 (MJ/kg)[62]
Polyethylene	43.3
Polypropylene	42.7
Pine wood[63]	18.5
Pine, red	12.9
Pine, white – Southern	13.6
Maple, hard	11.7
Oak, red	11.4

As plastic has become an increasingly large fraction of warehouse contents, studies and experience have shown that fires involving high proportions of plastics relative to wood can be harder to control than fires involving primarily wood, given similar warehouse fire prevention systems.

NFPA 13 Requirements for Plastic Pallets without Flame Retardants

NFPA 13 covers requirements for sprinkler system design (in relation to building design), storage organization and management, as well as assessment of the risks of warehouse contents, including pallets. The standard establishes requirements for the management of potential risks from non-flame retardant plastic pallets that are more stringent than those for wood pallets for two different situations in a warehouse:

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[61] The standard for flammability of wood pallets was established using red oak. As the table shows, however, the differences between woods are significantly less than the differences between any of the woods and either PE or PP. FAA, “Thermal Analysis of Polymer Flammability” (FAA Table 4), DOT/FAA/AR-07; Mark Dietenberger, “Ignitability of Materials in Transitional Heating Regimes,” U.S. Forest Service, TreeSearch, http://www.treesearch.fs.fed.us/pubs/7018; Richard N. Walters et al, “Heats of Combustion of High Temperature Polymers,” http://www.fire.tc.faa.gov/pdf/chemlab/hoc.pdf; *The Fire Safety Handbook,* US Department of Agriculture, Forest Service, Forest Products Laboratory.

[62] MJ/kg refers to megajoules per kilogram.

[63] *The Fire Safety Handbook* published by the US Department of Agriculture, Forest Service, Forest Products Laboratory, references heat release factors for soft woods and hardwoods.

- Stored commodities on pallets.[64]
- Empty ('idle') pallets.

Maine follows the NFPA 13 standards[65] at the state level, and most localities have also incorporated them by reference into their ordinances. For the most part, the local ordinances incorporate NFPA 13 without changes. A few localities have included additional requirements (e.g., specific requirements for areas of buildings requiring additional sprinkler protection), but none that bear on the use of plastic pallets. In addition, Maine has adopted the International Building Code (IBC), which becomes mandatory for all Maine communities in December 2010.[66]

Non-Flame Retardant Plastic Pallets with Commodities

In determining the levels of fire protection required for products stored in warehouses, NFPA classifies commodities on the basis of the threat they pose once ignited. The categorization system includes four commodity classes (Class I through IV, with Class I representing the lowest risk) plus an additional categorization of plastics commodities (Group A through Group C). Cartoned, unexpanded Group A plastic products pose the highest fire risks and are covered in Class IV, while Group B & C plastic products are covered in Classes III & IV. (See Class summaries and examples in Table 2.3).

While commodity classes are only one of the factors affecting warehouse fire protection requirements, an increase in the classes of commodities typically stored in a warehouse may require an increase in the level of warehouse fire protection, possibly involving changes such as increased density of sprinklers, changes in sprinkler placement, larger orifice sprinklers and/or increased water supply or pressure, particularly for older warehouses. The higher protection levels may apply to an entire warehouse or only to particular areas of a warehouse segregated for storage of higher risk commodities (e.g., a section of a grocery warehouse with products such as cooking oils in plastic containers). If

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[64] NFPA 13 defines a "commodity" as "the combination of products, packing material, and container that determines commodity classification." Section 3.9.1.6.

[65] Maine's Office of the State Fire Marshal currently uses the 2007 edition of NFPA 13.

[66] Maine Revised Statutes Annotated, Title 10, chapter 1103 (§§9721 -9725), as amended by Public Laws 2009, chapter 261. **http://www.mainelegislature.org/legis/statutes/10/title10ch1103sec0.html**. Maine has not adopted the International Fire Code (IFC), another international code on fire protection standards. Personal communication from: Eric Ellis, Maine Office of State Fire Marshal; Chief Robert Lefebvre, Fire Chief, Gorham, Maine, October 19, 2010; Captain David Jackson, Scarborough Fire Department, Fire Prevention Bureau, email October 15, 2010; Captain Charles Jarrett, Fire Inspector, Westbrook Fire Rescue Department, email October 14, 2010.

higher risk commodities are not segregated, the commodity rating determining the protection levels required is determined by the highest risk commodities stored.[67]

Table 2.3: Commodity Categories: Examples of Products/Materials from NFPA Automatic Sprinkler System Handbook[68]

Class I- Noncombustible product on wood pallet, in single-layer corrugated carton, or shrink- or paper-wrapped as unit load: *major appliances, canned foods, fresh fruit w/ non-plastic containers, meat products (bulk), milk, canned nuts.*	**Class II-**Noncombustible product in slatted wooden crate, solid wood box, multi-layered corrugated carton with or without pallet: *light fixtures in non-plastic cartons, pharmaceuticals in glass bottles or cartons, noncombustible liquids (e.g., ketchup) in plastic containers.*
Class III-Wood, paper, natural fiber or Group C plastic product with or without cartons, boxes, crates or pallets & up to 5% of Group A or B plastics: *aerosols, dried beans, packaged candy, cereal, clothing (natural fiber), wood products (furniture, toothpicks, doors), mattresses, paper products (books, newspapers, tissue products in cartons), diapers.*	**Class IV-**Products made from Group B plastics, free-flowing Group A plastic materials,[69] containing 5-15% (by weight) or 5-25% (vol) Group A plastics (including packaging): *ammunition; empty PET jars; waxed paper in cartons; rayon & nylon fabrics; natural rubber blocks in cartons; vinyl floor tiles in cartons; wax-coated paper cups or plates; pharmaceuticals in plastic bottles in cartons.*
Group A Plastics (highest risk): a*crylic, PET, polycarbonate, polyethylene, polypropylene, polystyrene, including products such as candles, butane lighters, foam plastic cushioning, stuffed foam toys, combustible or noncombustible solids in plastic containers, synthetic rubber.*	**Group B Plastics**: *cellulosics, chloroprene rubber, nylon, silicone rubber, fluoroplastics (ECTFE, FEP), nylon 6, natural rubber (not expanded).*
	Group C Plastics: *PVC, PVDC, melamine formaldehyde, phenolics, fluoroplastics (PCTFE, PTFE), urea formaldehyde.*

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[67] NFPA 13, section 5.6.1.2 on mixed commodities. The standard does allow for some extremely limited amounts of higher risk commodities to be dispersed among predominantly lower risk commodities in the warehouse.

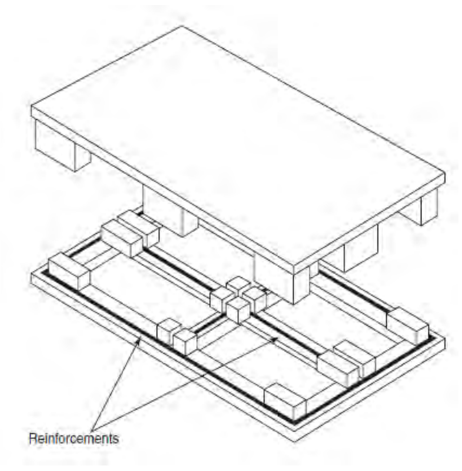
[68] NFPA, *Automatic Sprinkler Systems Handbook,* 11th Edition (2010), edited by James D. Lake. This *Handbook* includes both the text of NFPA 13 and interpretations and commentary on NFPA 13 provisions. See Tables A.5.6.3.1-4, section 5.6.4.

[69] NFPA 13 defines free-flowing plastic materials as, "those plastics that fall out of their containers during a fire, filling flue spaces, and create a smothering effect on the fire." Section 3.9.1.15.

What is the impact of plastic pallets without flame retardants on these commodity levels? Polyethylene and polypropylene, common polymers for plastic pallets, are listed as Group A plastics, and would be anticipated to contribute to the severity of any fire that broke out in a warehouse. As a result, if commodities are stored on non-flame retardant plastic pallets, the risk level of the commodity increases. There are two possibilities, depending on the construction of the pallet.[70]

- If the pallet on which the commodities are stored is made of unreinforced polypropylene (PP) or high density polyethylene plastic (HDPE), the classification of a Class I through Class IV commodity is increased one class. So a Class III commodity would become Class IV, and a Class IV commodity would become a cartoned, unexpanded[71] Group A plastic commodity. Since there is no higher commodity risk level, there would be no increase for a Group A plastic commodity.
- Some pallets are reinforced with embedded steel rods to strengthen the plastic. If the pallet on which the commodities are stored is made of reinforced PP or HDPE, the classification of a Class I through Class III commodity is increased two classes. So a Class II commodity would become Class IV, and a Class III commodity would become a cartoned, unexpanded Group A plastic commodity. Once again, Group A is the highest risk classification, so a Class IV commodity would be classified as Group A.[72]

Exhibit 2.1: Cut-Away Image of Reinforced Plastic Pallet



Picture from NFPA, Handbook, p.62.

Since reinforcing rods in a plastic pallet are not visible, unreinforced PP or HDPE plastic pallets must be marked with a symbol indicating that they are not reinforced. Any pallet without a permanent marking or manufacturer's certification that it is unreinforced will be

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[70] NFPA 13, sections 5.6.2.2 and 5.6.2.3.

[71] Expanded (foamed or cellular) plastics are those plastics whose density is reduced by the presence of numerous small cavities dispersed throughout their mass.

[72] NFPA's higher commodity increase for reinforced plastic pallets is based on the results of Underwriters Laboratories (UL) fire tests of commodities on both reinforced and unreinforced PP and HDPE pallets. *Handbook*, p. 100. Possible explanations include that the failure of reinforced plastics to collapse leaves more surface area exposed to the fire and that the rods may conduct heat.

considered reinforced, and the commodity classification will be increased by two levels.[73]

Empty Non-Flame Retardant Plastic Pallets: 'Idle Pallets'

Empty pallets, often in stacks, waiting for commodity loads or shipment to another location, are called "idle pallets." Stacks of idle pallets pose a major fire challenge. According to the *Handbook* for NFPA 13:

> Idle pallet storage introduces a severe fire condition. Stacking idle pallets in piles is the best arrangement of combustibles to promote rapid spread of fire, heat release, and complete combustion…. Idle pallets create an ideal configuration for efficient combustion by presenting many surfaces for burning and many openings that provide an almost unlimited source of air. At the same time, the configuration shields much of the burning surfaces from sprinkler discharge. In addition, pallets are subject to easy ignition due to their frayed, splintered edges and typical dried out condition.[74]

Factory Mutual Insurance Company (FM) provides this assessment of the increased fire risk from idle pallets:

> It should be noted that the relative hazard or classification of a commodity is a function of both the material and its configuration. For example, a solid block of wood is relatively difficult to ignite and slow to burn. If, however, the wood is in a configuration that maximizes surface area and has parallel surfaces to encourage re-radiation and convection (e.g., idle wood pallets), it burns much more rapidly. The large amounts of heat released under such circumstances can result in a hazard beyond that normally associated with the primary material of the product: idle wood pallets are much more hazardous than Class 3 commodities, although wood products are generally considered Class 3 commodities.[75]

As with palletized products, NFPA 13 applies stricter requirements to storage of idle, non-flame retardant plastic pallets than to storage of idle wood pallets.

- Warehouses or manufacturing sites can store stacks of both kinds of idle pallets outdoors or in a detached building or structure, but the NFPA 13 *Handbook* recommendations suggest greater control may be necessary for stacks of idle plastic pallets.[76]

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[73] NFPA 13, section 5.6.2.3.1.

[74] *Handbook*, A12.12, 12.12.1, p. 546.

[75] Factory Mutual Global Property Loss Prevention Data Sheet 8-1, "Commodity Classification," p. 3.

[76] NFPA 13, sections 12.12.1.1 & 12.12.2.1. The *Handbook* differentiates between wood and non-flame retardant plastic pallets even for outside storage, providing different recommended distances from the

- For indoor storage, there are significant differences. For idle wood pallets, the standard specifies:
    - A range of possible combinations of sprinkler types and orifice sizes for different idle wood pallet stack heights and storehouse ceiling heights, starting with smaller orifice, standard response sprinklers for smaller storage heights and continuing through options for large orifice Early Suppression Fast Response (ESFR) sprinklers for higher storage heights;, or
    - Under the lowest rated sprinklers, 4-stack piles of idle wood pallets up to 6 feet high, separated from other piles by at least eight feet or 25 feet of commodity.
- For idle plastic pallets, the standard's more stringent options require either that:
    - Indoor storage be in a cutoff room;
    - Storage of idle plastic pallets without cutoff rooms should be limited to 2-stack piles of no more than four feet; or
    - Sprinkler protection for higher storage heights should be provided only by larger orifice Early Suppression Fast Response (ESFR) sprinklers.[77]

Potential for Management Practices to Provide Safer Alternative to Use of DecaBDE

For management of products on plastic pallets and idle plastic pallets, there are potential solutions for meeting the levels of fire protection mandated by NFPA 13 without requiring that the plastic pallets be made with flame retardants. The alternative lies in a combination of warehouse/sprinkler system design and best practices for management and organization of stored commodities and idle pallets.

For storage of products on plastic pallets, NFPA 13 specifies that if warehouses already meet sufficiently high standards for fire protection sprinkler systems, the one- or two-step increases in commodity classifications for products on plastic pallets no longer need to be considered.[78] Similarly, the allowable storage heights and warehouse ceiling

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building depending on the numbers of pallets in the stacks for wood, while stating only that consideration should be given to the heat generation potential of the materials in plastic pallets [Handbook, A.12.12.1.1]. The FM Global Data Sheet on "Idle Pallet Storage" (8-24) spells this difference out in more detail, specifying greater distances from the building and between stacks of pallets for plastic than wood pallet stacks of similar heights. FM Global Loss Prevention Data Sheet 8-24, Table 2.

[77] NFPA 13, section 12.12; Table 12.12.2.1; personal communication from Carl Wiegand, Fire Protection Engineer, National Fire Sprinkler Association, October 5, 2010. ESFR sprinklers are designed to respond quickly to the fire with enough water to suppress it before it can grow and spread.

[78] NFPA 13, section 5.6.2.5. "For ceiling-only sprinkler protection, the requirements of 5.6.2.2 [for commodity classifications with unreinforced plastic pallets] and 5.6.2.3 [for commodity classifications with

heights for indoor storage on the floor or in racks without solid shelves are the same for idle plastic pallets and idle wood pallets when protected with identical larger orifice ESFR sprinkler systems – systems designed to suppress a fire as it starts through a combination of very quick response and large volumes of water.[79]

Installing more effective fire protection sprinkler systems and following best management practices within a warehouse could provide a "safer alternative" for continued use of plastic pallets without using flame retardant plastic pallets with decaBDE. To what extent is this viable statewide solution for Maine or for warehouses nationally?

Some warehouses, particularly those built more recently, meet the required design criteria, either in particular areas of the warehouse or overall. But costs may be a limiting factor in installing the most advanced systems, particularly for older warehouses that would require retrofitting, but to some extent even for newer warehouses.

Sprinkler fire protection depends not only on the sprinklers' speed of response to the fire, but on other factors such as the size of the sprinklers' orifices, sprinkler density and orientation, and the availability of adequate water volume and water pressure. In addition to the higher costs for the larger orifice sprinklers, the added water demand for these systems may require installation of pumps to ensure adequate system pressure, or even installation of tanks to ensure the availability of a sufficient water supply.[80]

While warehouses that have installed sprinkler systems with the largest orifice sprinklers are relatively rare, there are several such warehouses in Maine – primarily in warehouses that have high piles of storage or the highest-risk plastic commodities. Such sprinkler systems are most frequently found in newer warehouses, partly due to changes in fire suppression technology. The use of ESFR sprinkler systems with larger orifices didn't emerge until the late 1980s and older warehouses are unlikely to have the most advanced systems. Even newer warehouses, or older warehouses that have

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reinforced plastic pallets] shall not apply where plastic pallets are used and where the sprinkler system uses spray sprinklers with a minimum K-factor of K-16.8."

[79] NFPA 13, Tables 12.12.1.2(c) and 12.12.2.1.

[80] For example, cheaper sprinklers can be in the range of $30-40 per sprinkler; while the largest orifice sprinklers for an ESFR system can cost several hundred dollars per sprinkler; personal communication from Carl Wiegand, National Fire Sprinkler Association; Ken Linder, Swiss RE, chair of NFPA Design Discharge Committee, 10-22-10; Eric Ellis, Fire Protection Engineer, Maine Office of State Fire Marshal, 10-1-10.

upgraded, may have compliant systems that aren't sufficient to meet the protection requirements for plastic pallets without flame retardants.[81]

In terms of providing an adequate alternative for fire protection against the risks from plastic pallets without flame retardants, the limitation is that a significant proportion of warehouses lack the required sprinkler protection systems throughout the entire warehouse and are unlikely to upgrade in the near future. These warehouses can take other steps (e.g., increased aisle width; outside storage of idle pallets) to reduce the fire hazard associated with the use of plastic pallets, but adherence to such practices alone is insufficient to offset the sprinkler system limitations for the purposes of compliance with NFPA 13. A number of warehouses have separate areas with adequate protection for the highest risk Group A plastics. They also may use non-flame retardant plastic pallets that can be segregated and stacked separately when idle for use in deliveries from the warehouse to their own stores. But for most of their storage area, any plastic pallets would need to be flame retardant.

For example, the Hannaford warehouse in South Portland has higher protection areas for products such as cooking oils in plastic containers. It uses nestable plastic pallets without flame retardants to send to Hannaford stores, and stores them in small stacks meeting NFPA requirements when returned from the stores. But inbound products from suppliers on plastic pallets that will be stored on racks before being re-palletized for delivery to stores must be on fire-retardant plastic pallets.[82]

There is a large market for non-flame retardant plastic pallets. A spokesman for Orbis estimated that only about 5% of the plastic pallets customers buy are flame retardant.[83] This market includes captive systems where the pallets will only be used internally in a fully-protected warehouse or manufacturing site, or only travel between sites, fully under the control of the company, that meet NFPA standards for high risk commodities.

But the open-pooled pallet market faces different conditions. Shipments on pooled pallets will be sent to many warehouses that, even though compliant with fire protection standards, are not adequate for protecting against the risks from plastic pallets without flame retardants. So advanced fire protection sprinkler systems and best management practices are a solution to part of the problem of finding a safer alternative for decaBDE, but not an answer for all situations.

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[81] Personal communication from Eric Ellis, Maine Office of State Fire Marshal; Carl Wiegand, National Fire Sprinkler Association.

[82] Personal communication from Al Hussey, Warehouse Manager, Hannaford Warehouse, South Portland, Maine, September 13, 2010.

[83] Personal communication from Curt Most, Sales Manager, Plastic Pallets, Orbis Corporation, September 21, 2010.

Plastic Pallets with Flame Retardants

The other alternative provided by NFPA 13 for managing the fire risks from plastic pallets is that they be made with flame retardants and pass approved tests to demonstrate that their fire risk is equivalent to or less than that posed by wood. With respect to increased commodity classifications, section 5.6.2.6 states:

> The requirements of 5.6.2.2 [for unreinforced plastic pallets] and 5.6.2.3 [for reinforced plastic pallets] shall not apply to non-wood pallets that have demonstrated a fire hazard that is equal to or less than wood pallets and are listed as such.

For storage of idle plastic pallets, NFPA section 12.12.2.1(6) states:

> Indoor storage of non-wood pallets having a demonstrated fire hazard that is equal to or less than idle wood pallets and is listed for such equivalency shall be permitted to be protected in accordance with 12.12.1 [protection standards for wood pallets].

Two organizations provide testing to determine whether a plastic pallet may be considered equivalent to wood under NFPA 13. These are the Underwriters Laboratory (UL), a non-profit consensus-based standards organization, and Factory Mutual (FM), an ANSI-accredited standards developing organization active in both fire protection insurance and testing. The relevant testing standards are:

- UL 2335, Standards for Fire Tests of Storage Pallets.
- ANSI/FM 4996, American National Standard for Classification of Idle Plastic Pallets as Equivalent to Wood Pallets.

A company with a flame-retardant plastic pallet must put its pallet through large-scale fire tests to determine whether it performs as well as a wood pallet with respect to specific predetermined parameters. These tests are complex and costly, and designed to determine not only material attributes, but the effect of fire dynamics on large numbers of such pallets in a setting that replicates some of the factors that could determine fire risks in an actual warehouse setting.

Exhibit 2.2: Idle Pallet Fire Test[84]

The tests have both similarities and differences:[85]

- UL 2335 requires both idle pallet and commodity storage tests. The idle pallet test provides two alternative arrangements of 12 foot high stacks (6 or 14 stacks) of pallets that are tested for response with uniform firing and sprinkling. The commodity storage test (actually a sequence of three tests) involves testing a specified Class II commodity on eight pallets on 2-level racks (a 2x2x2 arrangement). The test is conducted three times with different water discharge levels (from .11 to .31 gallons per minute per square foot). Test results are measured against specific required acceptance criteria.
- FM 4996 tests 16 stacks of idle pallets arranged on 2-level racks (a 2x4x2 arrangement); the inside four stacks on each level are the pallets being tested (2x2x2), while outside stacks on each row and level are wood pallets. The pallets being tested have to perform as well as, or better than, the measured criteria for wood pallets, and may not exhibit "excessive melting, dripping or pooling." In addition, specimen sheets of the pallet materials are subjected to additional fire tests, both without and with "accelerated weathering" testing (a six week

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[84] "Material Handling Pallets: Regulatory Landscape," Presentation by Bruce Torrey, iGPS at the University of Massachusetts at Lowell, June 17, 2010.

[85] For more detailed information on the design of the tests, arrangements and numbers of pallets, etc., see the standards.

> process of exposure to UV light and condensation), to determine if such weathering results in adverse effects on the fire mitigation attributes of the material. FM 4996 does not include a test of plastic pallets with commodities.

For many, these two tests appear to be accepted as roughly equivalent. The handbook published by NFPA to provide explanation and commentary on NFPA 13 states (though it is important to note that, as stated in a notice at the beginning of the handbook, "the commentary and supplementary materials in this handbook are not a part of the NFPA Document and do not constitute Formal Interpretations of the NFPA…."):

> "Plastic pallets present a unique challenge for sprinkler protection. Recent studies and product development, along with significant fire testing, have shown that some plastic pallets have been tested and have demonstrated a fire hazard that is equivalent to or less than the fire hazard presented by wood pallets. Plastic pallets meeting these requirements are specifically listed as such. The requirements for adjustments in the commodity classification due to the use of different types of plastic pallets are based on UL 2335, *Standard for Fire Tests of Storage Pallets*, and ANSI/FM 4996, *American National Standard for Classification of Idle Plastic Pallets as Equivalent to Wood Pallets*, large-scale calorimeter tests. Listed plastic pallets are available that exhibit fire performance similar to that of wood pallets in these tests and can be treated as equivalent to wood pallets for commodity classification …."[86]

A spokesman for the Maine Office of State Fire Marshal stated that approval under either standard would be sufficient to meet the NFPA 13 requirement for demonstrating a fire hazard that is equivalent to wood.[87]

But the adequacy of the FM 4996 test for meeting these criteria is disputed. A fire protection consultant emphasized that the Handbook, although published by NFPA, is not definitive, and commented that the lack of a commodity test as part of the FM 4996 testing regimen is a weakness. He felt that Factory Mutual's requirement for greater sprinkler density in warehouses they insure makes FM 4996 sufficiently protective for those warehouses, but that plastic pallets meeting only the FM4996 standard managed the same way as wood pallets in warehouses not insured by FM would leave those warehouses vulnerable to greater fire risk.[88]

The lack of a definitive consensus on this issue was summarized by the chair of one of the relevant NFPA committees: "A product that is UL listed or FM approved would meet

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[86] *Handbook*, p. 100.

[87] Personal communication from Eric Ellis, Maine Office of State Fire Marshal, October 1, 2010.

[88] Personal communication, Jesse Beitel, Hughes Associates, Inc., December 2, 2010.

the definition of Listed per in section 3.2.3 of the standard." But he added: "Note that the definition includes the phrase 'list published by an organization that is acceptable to the authority having jurisdiction....' As a result some AHJs [Authorities Having Jurisdiction] may accept both and some may not."[89]

Manufacture of Plastic Pallets and Approvals under UL 2335 and FM 4996

As evident from Table 1.5 (Chapter I), only a small number of manufacturers, even among those who manufacture plastic pallets, are engaged in producing flame retardant plastic pallets, or in exploring opportunities for using flame retardants other than decaBDE with plastic pallets. As the above summary makes clear, developing and marketing a flame retardant plastic pallet requires, in addition to substantial R&D and bench testing, a significant investment in an extensive testing and evaluation process. The total cost for the full-scale testing required to achieve either the UL 2335 Classification 'listing' or the FM 4996 Approval 'listing' runs approximately $100,000. Even an idle pallet test for R&D purposes might cost $10,000.[90]

While a great deal of the relevant information is proprietary, Table 2.4 below provides a summary of publicly available information on current approvals and pending tests under both UL 2335 and FM 4996. One unusual entry in the table is that involving the listing of the CHEP wood pallet under FM 4996. Some of the CHEP pallets (less than 20%), while primarily made from wood, use a wood composite with a plastic resin for the pallet's nine blocks. Under NFPA 13, the presence of the plastic resin requires that the pallet be listed as an approved pallet.[91]

From a fire prevention perspective, it is clear that decaBDE has been effective in enabling plastic pallets to meet the NFPA 13 flame retardant standards. But with the combination of state phaseouts and US EPA's voluntary agreement with industry to end all sales of decaBDE in the US by the end of 2013, several pallet manufacturers are in the process of assessing and developing alternatives. The following Chapters will review what has led the pallet manufacturers to consider decaBDE an effective choice, and the efforts to develop safer alternatives that can be used to produce pallets that meet both performance and fire protection requirements.

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[89] Personal communication, Kenneth Linder, Swiss Re; chair of the NFPA Design Discharge Committee, email, November 29, 2010.

[90] These estimates were provided by Bruce Torrey, Vice President, Technology at iGPS, email to Ken Soltys, Pure Strategies on November 22, 2010.

[91] The NFPA 13 requirement is based on its definition of a "plastic pallet" in section 3.9.1.21 of the standard: "A pallet having any portion of its construction consisting of a plastic material." Personal communication from David Deal, Director Product Services and Industry Affairs, December 6, 2010.

Table 2.4: Manufacturers of Flame Retardant Plastic Pallets [92]

Manufacturer	Pallet Type	Polymer Type	Flame Retardant in Currently Listed Pallet	FM	UL	Status of Development of Pallet with Alternative Flame Retardant
ORBIS	Rackable/ Stackable Nestable	PE	DecaBDE & Sb_2O_3[93]	Yes	No	waiting for large fire test
Plastics Research	Rackable	No Info	No Information	Yes	No	
Polymer Pallets	No Data	PVC		No	Yes	
Polymer Solutions International	Rackable/ Stackable Nestable	HDPE	DecaBDE/Sb_2O_3	Yes	No	
Rehrig Pacific Company	Rackable, Nestable	PP	Magnesium Hydroxide	Yes	Yes	
Schoeller Arca Systems	Rackable/ Stackable	HDPE	DecaBDE/ Sb_2O_3	Yes	Yes	Under development
TMF Corporation	Rackable	PE	DecaBDE/ Sb_2O_3	Yes	No	waiting for large fire test
CHEP	Rackable/ Stackable	PP & HDPE	Proprietary phosphorus-based	Yes	Yes	
CHEP Wood Pallet with wood/plastic composite blocks	Rackable/ Stackable	Wood	It doesn't need a flame retardant to pass the tests	Yes	No	

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[92] Data gathered from personal communications with Bruce Torrey of iGPS on 8/17/2010; Curt Most of ORBIS on 9/21/2010; Amy Lander of Rehrig Pacific on 9/7/2010; Debbie Bergen of TMF on 9/7/2010. While the new Orbis pallet uses some form of non-halogenated flame retardant, it is not certain whether the new TMF pallet uses a non-halogenated flame retardant or an alternative (non-decaBDE) brominated flame retardant.

[93] Decabromodiphenyl ether (decaBDE) is almost always used in combination with antimony trioxide (Sb_2O_3).

Chapter III: Balancing Pallet Performance & Flame Retardant Goals

In developing, over the last decade, plastic pallets that could be used interchangeably with wood pallets in any warehouse setting, designers and manufacturers have focused on balancing physical performance characteristics and flame retardance. As evidence of the environmental and human health risks of the flame retardant in the favored combination of HDPE and decaBDE has accumulated, the need for ensuring reduced toxicity of the components of plastic pallets has become an additional factor in the required balance. Chapter VI addresses the toxicity issues related to potential fire retardant additives. Chapters III-V discuss the challenges involved in addressing the other parts of the balance – combining flame retardant and pallet performance goals.

Reasons Why Pallet Manufacturers Selected the Flame Retardant DecaBDE

"It performed significantly better than any other flame retardant on the market at that time, including other brominated products. It was the only product that needed less than 10% of the additives to get the results needed, which included weight, modulus retention, impact retention, processing (injection, extrusion, forming, welding). Another factor was availability (industry capacity) as well as cost."
Bruce Torrey, iGPS

Reducing Fire Risks of Plastic Pallets [94]

What are the major flame retardant technologies and how do they work?

There are three elements required for a fire. They are fuel, oxygen, and energy or heat. These three elements comprise the classic "fire triangle" (see Figure 3.1). This simplified representation of the combustion process has been used throughout the flame retardant industry literature for many years.

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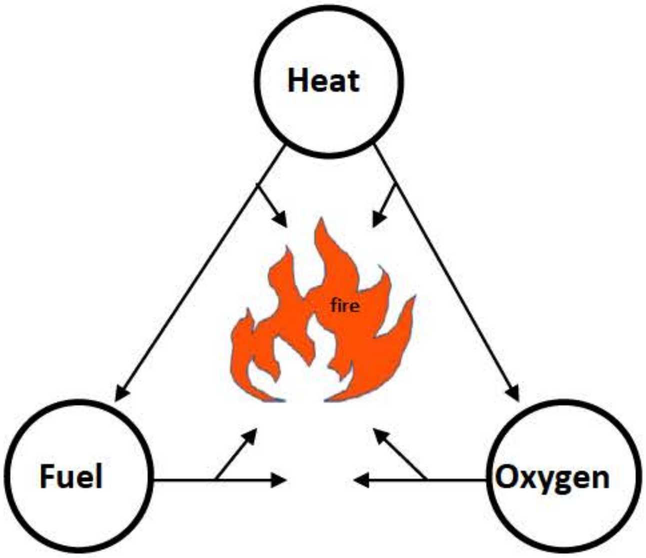
[94] Both this section and the following section ("Pallet Performance Characteristics") of this chapter prepared for this report by James Innes & Ann Innes of Flame Retardants Associates.

Figure 3.1: The Classic "Fire Triangle"



It may help to envision a burning candle. When one asks why the candle continues to burn once lit, the answer can be found in the fire triangle. Wax, the material of which the candle is made, is the fuel. The wax, which is melted by the flame heat, migrates up the wick and is burned or pyrolized (chemically changed) at high temperatures. The gases which result continue to undergo chemical reactions in the flame, components of which eventually interact at even higher temperatures with oxygen at the outer edge of the flame. As long as the fuel (candle wax) remains and the air (oxygen) is present at the candle flame, burning will continue.

So the three elements of the triangle are actually the critical determining parameters for fire. Fuel is contributed to any fire by the article or articles being burned. Important factors for fuel in the real world include aspects such as the types of furniture and their position in the room, other furniture characteristics such as size, shape, density, surface properties and other physical or chemical properties. The latter include heat of combustion, thermal conductivity, and ignition temperatures.

Oxygen is a required element for combustion. If one pinches the burning candle wick with fingers or uses a candle snuffer, the oxygen is removed from the candle burning scenario and the flame goes out. Energy or heat is generated during the chemical reactions occurring in the flame and at the flame-oxygen interface and, by interaction with the fuel, continues the burning process. Important factors include the proximity to the fuel and the chemical components generated from the combustion and decomposition of the fuel.[95] Combustion or burning continues as long as the three triangle elements are present in sufficient quantity. If any one of these elements is removed or interfered with, the combustion process is disrupted. This removal or interference is the practical objective of flame retardants. Over several decades, researchers in the flame retardant industry have developed a large portfolio of flame retardant products which attack one or more of the three triangle elements.

The Three Major Flame Retardant Technologies

There are many flame retardant products under development and in commercial use today. Most of the older commercial flame retardant products can be classified into three major flame retardant technologies. The first of these technologies is also the oldest and could be described as the “workhorse” flame retardant technology. Halogenated flame retardant technology includes a large number of products which typically contain bromine, chlorine, or sometimes both. Specific product examples include Decabromodiphenyl oxide (decaBDE), Tetrabromobisphenol A (TBBA), and Hexabromocyclododecane (HBCD).

The action of halogen flame retardants during combustion is complicated. They are known to act mostly in the gaseous or vapor phase. During the combustion process, a persistent supply of chemical free radicals (elements such as hydrogen and/or carbon-hydrogen with free electrons)[96] is generated. The flame retardant decomposes during the combustion process to generate halogen acid gas. It is this gas which interacts with the chemical radicals, essentially “trapping” them, and thereby interrupting the combustion process. This mechanism is sometimes referred to as radical trapping and corresponds to the disruption of energy (or heat) on the fire triangle. This is a simple explanation of a complex reaction.[97]

Halogen flame retardant products are almost always used in conjunction with other products called synergists. A synergist is defined as a product which, when used in combination with a flame retardant product, boosts the flame retardant performance to a level that is greater than that achieved if the respective flame retardant performance of the two products were simply added together. Synergists are used in specific ratios with the flame retardant product to maximize the flame retardant performance. The most well-known and widely used halogen flame retardant synergist is antimony

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[95] “International Plastics Flammability Handbook”, Jürgen Troitzsch, Carl Hanser Verlag, Kolbergerstr, 22, D-8000 München, Germany, 1983, p. 12-15.

[96] “Van Nostrand Reinhold Encyclopedia of Chemistry”, Fourth Edition, Van Nostrand Reinhold Company Inc., 135 West 50th Street, New York, NY 10020, 1984, p. 406.

[97] Additional details including alternative explanations are available in the literature. See Troitzsch, 1983, Op.cit. p.47.

trioxide. This synergist is thought to boost effectiveness of the flame retardant system by ultimately generating antimony trihalide, which also acts as a radical trap. Again, this is a simple explanation of what actually is a much more complex series of actions, all of which interfere with the combustion process.[98] Halogen flame retardant products are used in a wide variety of resins including polyolefins, polystyrenes, polyamides (nylons), polyesters and more.

The second major flame retardant technology is also currently the fastest growing segment and is comprised of products called metal hydrates. The most well-known flame retardant metal hydrate is aluminum trihydrate (ATH). Another metal hydrate flame retardant that is growing in use is magnesium hydroxide or $Mg(OH)_2$. The interest in the magnesium hydroxide flame retardant product can be attributed at least in part to the current industry focus on environmentally friendly flame retardants. These metal hydrate flame retardants function by releasing water vapor in product specific temperature ranges. That reaction leads to several effects which interfere with the combustion process. The release of water vapor acts to cool the substrate by absorbing heat. In addition, an insulating metal oxide layer is formed on the substrate, and a dilutive effect is also produced in the flame front. Metal hydrate flame retardants interfere with at least two of the three triangle components - heat and fuel.[99] Metal hydrate flame retardants are also used in a variety of resins including polyolefins, olefinic elastomers, EVA (ethylene-vinyl acetate), PVC and some epoxies.

The third major flame retardant technology includes products containing phosphorus. Common FR products include ammonium polyphosphate (APP), red phosphorus, and other phosphates and phosphonates. Well-known and well-used products of the phosphate ester type include resorcinol diphosphate (RDP), and bisphenol A diphosphate (BDP). The flame retardant mechanism for phosphorus-based products is largely perceived to be a char-forming mechanism following the decomposition to phosphoric or polyphosphoric acids during the combustion process. However, depending on the specific phosphorus flame retardant product and the resin substrate type, the actual flame retardant mechanism can be multifunctional and may also include vapor phase activity (like that of the halogen flame retardants) and/or cross-linking mechanisms.[100]

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[98] Troitzsch, 1983, Op.cit., pp. 48-49.

[99] Again the interested reader is referred to the literature for further details. See "Compounding metal hydrate flame retardants", Jim and Ann Innes, Plastics Additives & Compounding, Vol. 4, Issue 4, Elsevier Advanced Technology, PO Box 150, Kidlington, Oxford, OX5 IAS, UK, April 2002, p.23.

[100] Consult FR industry references for further details. See: "Plastics Flammability Handbook", 3rd edition, Jürgen Troitzsch, Carl Hanser Verlag, Munich Germany, 2004, pp.133-153, p. 533.

Phosphorus containing flame retardant products are used in resins including PVC, acrylonitrile butadiene styrene (ABS), PC/ABS, polyamides and polyphenylene oxide (PPO). The amount of phosphorus compound (with synergists and/or other additives) that must be loaded into the polymer to achieve flammability performance depends on the polymer type.

Although the above are considered the three major flame retardant technologies, there are of course a number of flame retardant products which do not fit into those groups. These include products based on nitrogen, sulfur, boron, graphite, and silicone.

Smoke suppressants are a separate class of product often discussed with flame retardants. Smoke is composed of water, carbon particles, ash, soot and other combustion by-products which are contained in combustion of gas and air. This collection of components is perceived by the human eye as smoke. Smoke suppressants are compounds which work to suppress the production of smoke during the combustion process. Metal hydrate and char-forming flame retardant products can be considered smoke suppressants in and of themselves. The metal hydrate products, by their nature and mode of action, produce lower smoke and the char formers effectively retain carbonaceous material in the solid phase (preventing the subsequent contribution to smoke production). There is another type of smoke suppressant which essentially works in flame retardant systems containing halogen flame retardant compounds. These include products based on molybdenum and zinc compounds. Molybdenum oxide and ammonium octamolybdate (AOM) are among the older, more widely recognized products. Such products work in the solid phase through cross-linking and other modifications to the pyrolysis process. All of these work to keep the fuel in the solid phase.[101]

Finally, mention should be made of nanotechnology, the leading focus in flame retardant technology development today. Nanotechnology is seen in a variety of industries and applications, not just in flame retardants. Nano is usually defined as one-billionth (or 10^{-9}). In flame retardant technology, nano does not mean one billionth. Nano composite polymers are polymers with a different internal structure such as alternating nanometer-thick layers of organic and inorganic materials. These frequently impart flame retardancy to the systems in which they are incorporated. This technology is relatively new and will not be applicable to the subject of flame retardant plastic pallets. However, the exciting aspect of this nanotechnology in flame retardant

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[101] "Flame Retardants in Commercial Use or Development for Polyolefins", Edward Weil, Sergei Levchik, Journal of Fire Sciences, Vo. 26, No. 1, 5-43, January 2008, Sage Publications Ltd., 1 Olivers Yard, 55 City Road, London EC1Y 1SP, UK, Sage Journals Online, http//jfs.sagepub.com.

technology is the improvement in physical and mechanical properties often found in addition to possible improvement in flammability. These improvements are highly valued as the use of flame retardant additives in thermoplastic formulations frequently adversely affects physical and mechanical properties of the formulation. Indeed one of the tricks in successfully using flame retardant additives is how to balance the opposing effects of increased flammability performance and decreased physical/mechanical properties.

Pallet Performance Characteristics[102]

Pallets must be strong enough to support the loads being placed on them, hold the loads in a stable fashion during transport, fit through doors of varying sizes, be durable and impact-resistant, be reusable in a significant way, stack easily, and pack tightly inside intermodal containers or trucks/vans to maximize the shipping space inside the container. To summarize: five interactive design parameters are usually of importance in designing a pallet: strength, stiffness, durability, functionality and cost. These are interactive and the trick is balancing these properties. Maximizing just one will have an impact on the others.

The key to a successful flame retardant plastic pallet is to design a pallet meeting all the necessary physical properties and the required flammability performance by using the proper choice of polymer resin, flame retardant system, and other additives (colorants, impact modifiers, etc.). All of these pallet requirements must be met with a formulation that is not cost-prohibitive. Flame retardancy standards and testing have already been reviewed. Cost will be discussed in the next chapter. Immediately below, the remaining four properties will be briefly discussed.

Strength generally refers to the amount of weight a pallet can carry both at rest and in motion during shipping and in storage environments. Pallets can be strength-tested using standardized pallet testing methods. One such method is ASTM D1185-98a (2009), Standard Test Methods for Pallets and Related Structures Employed in Materials Handling and Shipping. There are several test protocols in this standard including conditioning requirements, static stiffness and strength tests, and dynamic tests of structural reliability. See Table 3.1 for a summary of some of the applicable test criteria for the static tests, as well as for some of the dynamic tests. For the best understanding

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[102] This section of the chapter, as the preceding section, prepared for this report by James Innes & Ann Innes of Flame Retardants Associates.

of these test protocols, the reader is referred directly to the standard in its entirety[103]. Additionally, there is a design program (PDS –Pallet Design System) developed by Virginia Tech Pallet Laboratory. This is thought by many to be the best predictor of strength for wood pallets[104].

Table3.1: Key Pallet Performance Properties[105]

ASTM 1185 "Standard Test Methods for Pallets and Related Structures Employed in Materials Handling and Shipping"

Static Test	Test Load Level	Maximum Allowable Deformation After 2 hours under test load	Maximum Residual Deformation after 1 hour	Test	Significance to User
Compression tests of deck spacers	1.1xMR	0.160 inches (4 mm)	.06 inches (1.6 mm)	ASTM 1185 Test 8.3	Measures the total load a pallet can support without bulging or deforming -"Stack Load Capacity"
Bending tests on pallets	1.25xMR	0.019xL_1 or L_2[106]	0.0075xL_1 or L_2[106]	ASTM 1185 Test 8.4	A measure of the total load a pallet can support when suspended between two beams of a rack. – "Rack Load Capacity"
Bending tests on pallet decks on 48" span Top Bottom	1.1xMR[107] 1.1x(M-1)R	0.015xL_3[108]	0.0053xL_3[108]	ASTM 1185 Test 8.5	Measures the total loads that the pallet deck can support when the top or bottom decks are suspended by slings or a forklift.

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[103] ASTM D1185-98a(2009) "Standard Test Methods for Pallets and Related Structures Employed in Materials Handling and Shipping, http://www.astm.org/Standards/D1185.htm

[104] Clarke, John. "Balance Your Pallet Design" in *Your Machinery Source*, Feb. 2002, Pallet User Education Series: Pallets & Packaging 101, http://www.palletenterpirse.com/educate.asp.

[106] When supporting pallets under the top deck, the span between supports representing the largest deformation shall be used. "Standard Test methods for Pallets and Related Structures Employed in Materials Handling and Shipping," ASTM D1185 – 98 (reapproved 2009), p.11.

[107] M is maximum number of unit loads stacked one on top of another during pallet use and R is a preliminary safe working load which is the average failure load adjusted to an appropriate safety level. (For wood pallets, this adjustment factor is often o.35).

[108] L3 is the longest space between deck spacers.

Dynamic Tests	Test Results	Test	Significance
Free fall drop tests	The pallet has failed the test if the observed damage in any pallet tested affects pallet rigidity, strength, or functionality.	ASTM 1185.9.3 Fall Drop Test from 40”	Measures the resistance to breakage when dropped from prescribed heights
Incline impact tests	The pallet has failed the test if the observed damage in any pallet tested affects pallet rigidity, strength, or functionality.	ASTM 1185.9.4 Incline Impact Tests on Pallet Deck Edges, Blocks or Posts, and Stringers—	Measures the resistance to breakage when a pallet is struck at angle by a fork lift
Vibration tests	The pallet has failed the test if the observed damage in any pallet tested affects pallet rigidity, strength, or functionality.	ASTM 1185.9.5 Vibration Tests on Loaded Pallet and load free pallet	Measures the resistance to breakage when subjected to vibrations on a vibration table

Stiffness is the ability of the pallet to resist deformation under load. With plastic, this can be a critical property to check, as plastic is renowned for having a “creep” factor; it moves or flows over time. Adequate pallet deck thickness can control this property and obtain the desired stiffness. Testing must be done to confirm adequate stiffness for the pallet’s intended use.

Durability refers to a pallet’s ability to retain integrity and remain whole and functional throughout its use life. The intended life can vary depending on the pallet’s purpose. Some need more durability while others need far less. Standardized test methods are available to assess this property.

Functionality: A pallet must be able to protect its load throughout the material handling process. Specific factors that are important in assessing the property of functionality include: opening heights between the top and bottom decks of the pallet; pallet weight; and deck friction. Standardized tests are available to help assess this property and include Material Handling Industry of America standard MH1-2005, Pallets, Slip Sheets, and Other Bases for Unit Loads[109].

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[109] MH1-2005, “Standard on Pallets, Slip Sheets, and Other Bases for Unit-Loads”, Material Handling Industry of America, www.mhia.org.

Impacts of Flame Retardants on Pallet Performance

When flame retardants are added to the polymer used for making a plastic pallet, they don't just reduce the pallet's flammability. They can affect the strength, stiffness, durability and functionality of the pallet as well. Using information on non-halogenated flame retardants recommended for use in plastic pallets by a variety of sources, this section provides some examples of the challenges in simultaneously meeting flame retardant and performance goals.

All but two of the plastic pallets currently on the market in the U.S. are made with polyethylene, polypropylene, or high density polyethylene (polyolefins).[110] Since that polyolefin polymer represents the bulk of the plastic compound used to make pallets, it is the main contributor to the flammability of the plastic. It is this flammability that the flame retardant must suppress in order to render a pallet equivalent to wood. Therefore, the search for alternatives has focused on flame retardants that have a history of being used in plastic products based on polyolefins.

The flame retardants in Table 3.2 were selected for consideration in this alternatives assessment on the basis of being recommended for, or used in making, a range of flame retardant plastic products. Some are already in use in plastic pallets. Examples of the use of non-halogenated flame retardants in plastics for other applications include:

- Clothing such as children's nightwear, hospital linen and technical fire-resistant textiles for fire fighters and military personnel;
- Electrical and electronic equipment such as TV and computer housings, household appliances, industrial electrical installations, and portable electronics;
- Transportation vehicles (airplanes, ships, trains, cars); and
- Wire and cable.

Table 3.2 contains the chemical name of the flame retardant, its Chemical Abstracts Number (CAS #), the manufacturer and product names, and the polymers used with these flame retardants. The column for "% Estimated for FM/UL Compliance " contains estimated concentrations of the flame retardant required to produce a plastic compound that could potentially be molded into a UL 2335-certified or FM 4996-approved plastic pallet. The last column contains references and some comments by the authors of those assessments.

Note that some of the flame retardants identified in this table are not used as the sole flame retardant additive. Almost all flame retardants are used in combination with

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[110] See Table 1.5, Chapter 1.

synergists or co-flame retardants that supplement the action of the prime flame retardant with complementary mechanisms. For example, US Patent 7,252,041 "Flame retardant polyolefin pallets and flame retardant master batch for their production" describes a combination of magnesium hydroxide, aluminum trihydrate and zinc borate used with polypropylene to make a flame retardant plastic pallet. DecaBDE is almost always used with antimony trioxide as a synergist. Whenever the information is available, candidate flame retardants should be evaluated with the recommended synergist and/or supplemental retardants. Keep in mind that these synergists and supplemental flame retardants also have an effect on the physical properties of the plastic compound.

Table 3.2: Estimated % Requirements of Non-Halogenated Flame Retardants for Plastic Pallets

Flame Retardant Chemicals	CAS #	Manufacturer/ Product Name	Polymer Applications	% Estimated For UL/FM Compliance	Source of Estimates[111]
Inorganic Metal Compounds					
Magnesium Hydroxide Particles treated with stearic acid or vinyl triethoxy silane to yield magnesium stearate and magnesium vinyl silane	01309-42-8	Martin Marietta Magnesium Specialties/ Mag Shield S	Polypropylene	23%	
ATH - Aluminum tri-hydroxide Particles treated with stearic acid or vinyl triethoxy silane to yield magnesium stearate and magnesium vinyl silane	21645-51-2	Alcoa Aluminum Aluminum Trihydrate	Polyethylene	>25%	
Zinc Borate Primarily used in conjunction with other flame retardants	138265-88-0	US Borax Firebrake ZB	Polypropylene	Used w/Magnesium hydroxide & ATH	
ATH/Mag Hydroxide/Zinc Borate	Mixture	Proprietary masterbatch	Polypropylene	12-25% Mag Hydrox 2-5% ATH 2-5% Zinc Borate	United States Patent: 7252041 Flame retardant polyolefin pallets and flame retardant master batch for their production

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[111] Source of information on concentrations of flame retardants, unless otherwise identified, James and Ann Innes of Flame Retardant Associates.

Flame Retardant Chemicals	CAS #	Manufacturer/ Product Name	Polymer Applications	% Estimated For UL/FM Compliance	Source of Estimates[111]
Phosphates					
APP Ammonium Polyphosphate	6833-79-9	Clariant USA Exolit AP 422	Polyethylene, Polypropylene & HDPE	>12 %	
APP Ammonium Polyphosphate (ammonium poly-phosphate + 6-10 % melamine synergists)	Mixture	Clariant USA Exolit AP 760	Polyethylene, Polypropylene & HDPE	10 - 30%	Exolit AP 760 MSDS
RP Red phosphorus (concentrates)	7723-14-0	Red Phosphorus NF Clariant	Polyethylene, Polypropylene & HDPE	>9%	Yields UL 94 V-2 NIST Fifteenth Meeting of the UJNR Panel on Fire Research and Safety
Trialkylated phenyl phosphate	Mixture	Phosphlex 71B	Modified polyphenylene oxides	Not available	Primarily used with NORYL® polymers
Bisphenol A Diphosphate	5945-33-5	Phosphlex	Modified polyphenylene oxides		Primarily used with NORYL® polymers
Amine phosphate salts					
Amino phosphate + amines + phosphates	Proprietary	JJAZZ	Polyethylene Polypropylene	30%- 40%	Combination of amine and phosphate gives added flame retardance JJAZZ MSDS. "Innovative and Novel Non-Halogen Flame Retardants" Nicholas A. Zaksek, Manager of Applications Research and Development, JJI Technologies (See Appendix VII).
Melamine cyanurate	37640-57-6	Ciba Metapur MC 350	Polypropylene	No recommendation available	On PINFA list but no history of being considered for pallets. PINFA - Nitrogen based flame retardants
Ethylene diamine phosphate (contains other proprietary amines)	14852-17-6		Polyolefins	No recommendation available	
Melamine polyphosphate	218768-84-4	Clariant Exolit AP 765	Polypropylene	>20%	Recommended by Clariant for injection molding grade polyolefins. Clariant Pigments & Additives - Exolit AP

The estimated levels of the flame retardants required to reduce the flammability of the plastic resins demonstrate a significant challenge in developing a range of effective replacements for decaBDE. The concentration of decaBDE in plastic pallets that are certified by UL 2335 and approved by FM 4996 is 5-10% plus 1-3% antimony oxide. But the estimated concentrations to achieve the same level of flame retardancy with the non-halogenated flame retardants in Table 3.2 (except for red phosphorus and possibly APP with synergists) are between 20 – 30%.

The incorporation of flame retardants, including decaBDE, into a plastic compound adversely affects the physical properties of the plastic, and consequently adversely affects the performance properties of a plastic pallet. Since all but two of the candidate alternatives must be used at higher concentrations than decaBDE, some of the candidate flame retardants would be expected to have a greater effect on the physical properties of the plastic than decaBDE. To illustrate how a flame retardant affects the properties of a polyolefin, Table 3.3 shows how increasing concentrations of magnesium hydroxide affect HDPE's melt flow index and tensile strength – key factors in the processability of the polymer and the weight-bearing strength of a pallet. These data indicate that the melt flow index is adversely impacted by increasing concentrations of magnesium hydroxide. As melt flow becomes too low, it reduces processability of the polymer during manufacturing, and this will result in a slower rate of pallet production. The tensile strength, however, although affected, is not reduced to an extent that would be considered a problem.

Table 3.3: Effect of Magnesium Hydroxide on Properties of HDPE[112]

Magnesium Hydroxide % Concentrations	Melt Flow Index, grams/minute	Tensile Strength, Mpa[113]
0	7.0	23.0
35	5.4	24.9
40	4.0	24.7
45	2.2	24.3
50	1.2	23.0
55	0.8	22.5
60	0.2	21.8
65	0.1	20.0

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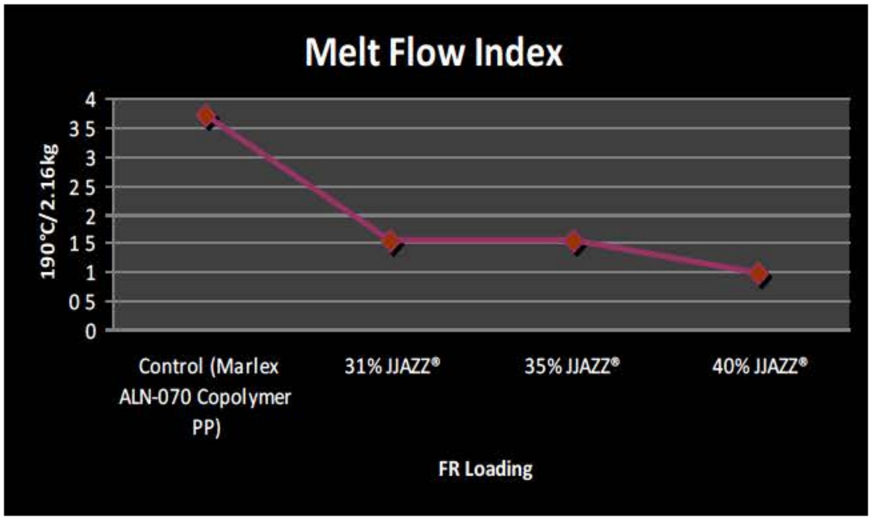
[112] "Compounding High Flame Retardant Chemicals Into Polymers" James Innes & A W Cox Flame Retardants Associates presented at Flame Retardant Chemicals Association 10/26/97

[113] Mpa is the abbreviation for the megapascal unit of measurement.

Another example of how non-halogenated flame retardants affect the physical properties of a plastic is shown by the graphs in Figure 3.2. They illustrate the deleterious effect of increasing concentrations of JJI's JJazz amino phosphate flame retardant on melt flow, impact resistance and flex modulus (a measure of stiffness/resistance to breaking) of a polypropylene with a Melt Flow Index of 7.[114] The graph of the Melt Flow Index shows how increasing the concentration of JJAZZ reduces the melt flow index of the polymer, just as in the previous magnesium hydroxide example. The second graph, Flex Modulus, shows that increasing the concentration of JJAZZ also is coincident with an increase in modulus, or stiffness. Pallets need to be stiff, but if excessively stiff, they break too easily. The third graph, Notched Izod, shows the plastic compound's brittleness; when the level of JJAZZ increases, far less impact is required to break the plastic. A brittle pallet can shatter when dropped or shocked by a fork lift Thus increased concentrations of the JJAZZ amino phosphate flame retardant are associated with reduced processability and increased stiffness and brittleness

Figure 3.2: Impacts of Amino Phosphate Flame Retardant on Properties of Plastic Polymer



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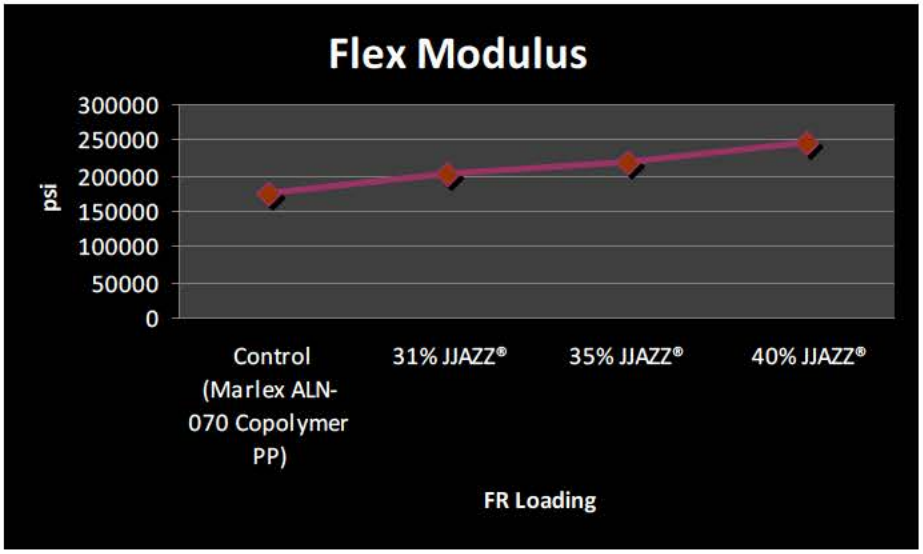
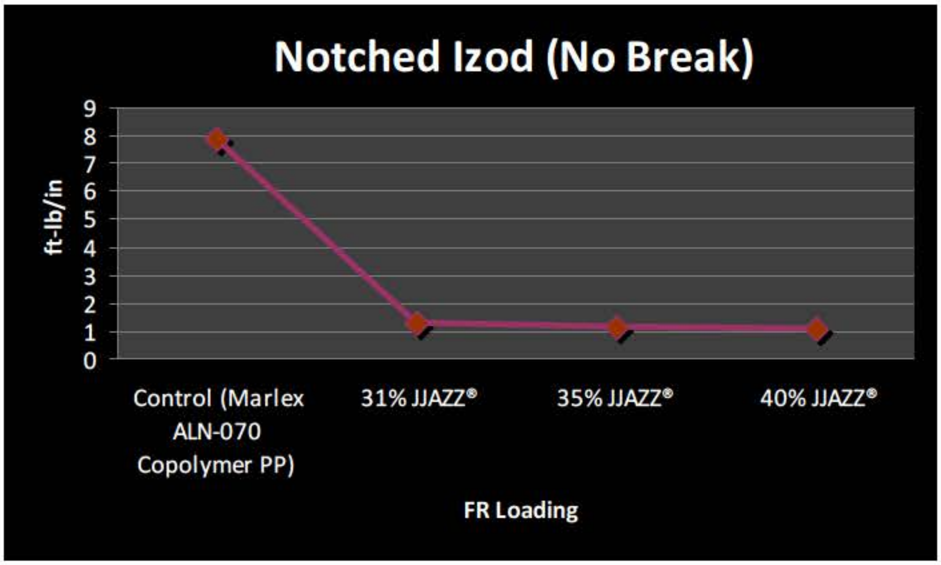
[114] "Innovative and Novel Non-Halogen Flame Retardants" by Nicholas A. Zaksek, Manager of Applications Research and Development, JJI Technologies.





Devising solutions to the technical difficulties of making a workable non-halogenated flame retardant pallet is a major task. But it is made even more challenging by the need to meet the cost constraints of a highly competitive market. We will explore this issue in the next chapter.

Chapter IV: Costs

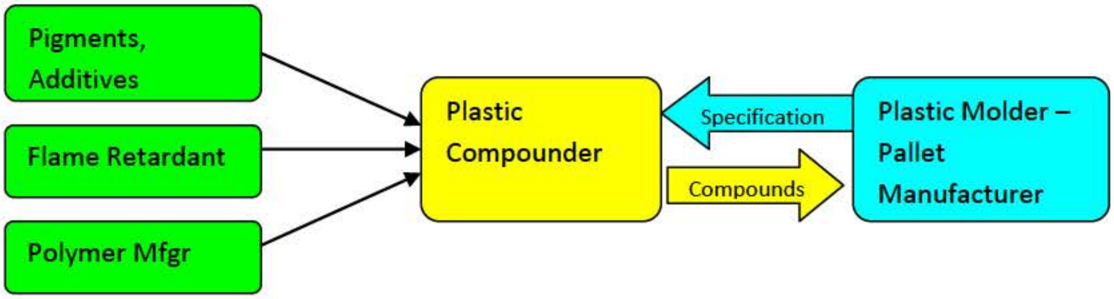
In designing a new plastic pallet with an alternative, non-halogenated flame retardant to replace the use of decaBDE, developers not only face an array of daunting formulation challenges in balancing the demands of flame retardancy and other physical attributes for a plastic pallet as discussed in the last chapter, but also major cost concerns. Cost pressures include both the development process itself and the ultimate cost of the pallet in the marketplace. This chapter will provide a brief overview of some of the roles and costs involved in the development process, and the interplay of cost and physical parameters in constraining the alternatives in the development of a non-halogenated fire retardant plastic pallet. One important bottom line is that a shipping pallet is not a premium-price product. The best pallet money can buy is likely to be far too costly for the real market. So developers need to balance not only the effectiveness of a flame retardant/polymer compound in reducing the pallet's flammability while maximizing essential strength, stiffness, durability and functionality goals, but to achieve this technical balancing act while recognizing that a pallet is a commodity product. Cost matters.

Costs for the new pallet include the costs of the development process, and the recurring costs built into the design and materials for the blend of flame retardants and polymers selected.

Costs in the Process of Designing and Developing a Plastic Pallet

Designing a new pallet and bringing it to market requires a large investment by the manufacturer. Figure 4.1 below depicts some of the key activities in design and production.

Figure 4.1: Pallet Manufacturing Flow Diagram



As Figure 4.1 shows, there are several contributors to the process of designing a new pallet. The pallet manufacturer, with the molding equipment that will be used to produce the pallet, sends a set of specifications for a flame retardant plastic pallet to the plastic compounder. The compounder develops a formula for the ingredients of the plastic *compound* containing polymers, flame retardant(s) and other performance enhancement additives that, when mixed in the proper proportions and molded, will produce a plastic pallet that meets the key pallet performance properties specified by the pallet manufacturer. For the compounder, the balancing act in meeting the manufacturer's specifications will involve finding a combination of ingredients that yields a plastic compound with physical properties that correspond to acceptable pallet performance characteristics shown in Table 3.1 of the last chapter. Table 4.1 shows the relationship between physical properties of the plastic compound and pallet attributes.

Table 4.1: Challenges for the Compounder: Balancing Physical Properties

Physical Properties	Definitions	Relationship to Pallet Attributes
Specific Gravity	The weight of a substance divided by the volume it occupies at a standard temperature and pressure	The higher the specific gravity the heavier the pallet. This is a critical pallet cost factor, and will be discussed in more detail in the next section of this chapter.
Modulus	A measure of stiffness or resistance to bending, determined by a bending test	Related to how a pallet withstands bending under stress -- a key property for indicating the "Rack Load Capacity"
Impact Resistance	The relative susceptibility of plastics to fracture under impact stresses applied at high speeds	Fracturing under impact stresses relates to brittleness; a pallet is tested for brittleness via a drop test.
Deflection	A measure of the deformation of a plastic under stress.	Deflection relates to the dimensional changes in a pallet when subjected to heavy static loads.
Melt Flow	Measure of the flow of a molten plastic under heat and pressure.	This is a key indicator of the processability of the plastic during the pallet manufacturing process.
Flame Resistance	Ability of a compound of flame retardant to reduce a polymer's flammability	Ultimately, the goal is to design a pallet that can pass the UL 2335 or FM 4996 tests.

As the graphs from JJAZZ illustrate (see Figure 3.2), the effects of the flame retardant may undermine the other needed attributes to varying degrees. There is no guarantee that a given flame retardant mixture will be effective at a low enough level to avoid under-cutting performance on the other attributes. Finding the right mix for a new, non-halogenated flame retardant, if successful, may involve a lengthy process of iterative testing. As the development process continues, there are a number of key hurdles, some of which have potentially high costs.

- After one or more promising candidate mixtures is developed, batches of compound will be made to make one or more pallets in the compounder's production mixing equipment and the pallet manufacturer's production molding equipment. If a compound successfully processes in the molding equipment, then the compounder will make a bigger batch of compound – enough to make 10, 20 or 50 pallets. This will test the compound's processability in production equipment. Ultimately, processability of a compound is a potentially significant cost issue, a matter of the maximum achievable production rate while maintaining product quality. For example, if a compound made with a nonhalogenated flame retardant were to have a production rate of 20 pallets/hour while a compound made with decaBDE had a production rate of 35-40 pallets/hour, then there would be a significant economic disparity.[115] This disparity would have to be compensated for with a lower price for other factors in pallet production.
- The best performers of the pallets made from a test batch of compound may be sent to UL for medium-scale idle pallet testing. This testing can cost as much as $10,000 for each iteration.[116]
- If a compound satisfies all of the criteria for making a flame retardant plastic pallet in production equipment, then a larger batch of compound is produced so the pallet manufacturer can submit the necessary number of pallets for the large scale fire tests which can cost as much as $100,000. Failure requires reformulation, going through many of the steps all over again.[117]
- If successful, the pallet manufacturer orders a small production run of pallets for test marketing. The test marketing program may fail to generate enough income to cover the costs of the pallets made for the program.

The development and testing process has many uncertainties and, at the end of the process, no guarantee of success. But the key cost parameter is more likely to be the recurrent costs of production built into the flame retardant/polymer compound used to make the pallet.

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[115] Personal communication with Bruce Torrey, iGPS, November 28, 2010. The production rate is based on producing 300,000 pallets per year operating 8,000 hours per year, or nominally 24/7. This was a hypothetical production rate supplied by iGPS to illustrate the effect of processability on production rate.

[116] Personal communication with Bruce Torrey, ibid.

[117] Personal communication with Bruce Torrey, ibid.

Materials and Pallet Costs

The Cost Factor and Flame Retardant Plastic Pallets[118]

A key property of plastic compounds that directly affects the cost factor is specific gravity. Specific gravity can be defined as the density (mass per unit volume) of any material divided by that of water at a standard temperature (usually 4°C). Standard industry practice is to use specific gravity as a measure of density. What does this mean? For a given volume of material, a plastic compound with a lower specific gravity will produce a part with lower weight; it takes fewer pounds of material to fill a mold to produce the part. A given amount of a plastic compound or formulation with a lower specific gravity will produce more parts than another formulation with a higher specific gravity. **Molds are filled on a volume basis, not by weight.** One of the resulting "tricks of the trade" is knowing that a less costly formulation which meets all the part's requirements across the board may simply not be economically attractive if its specific gravity is too high. In other words, needing more of the compound to fill the mold often wipes out the advantage of the lower cost per pound.

Comparing Flame Retardant Compounds

The data in Table 4.2 illustrate how various flame retardants affect the specific gravity of a plastic compound. The data was derived from assorted product information sheets and technical papers on flame retardants incorporated in polyolefins. For the purpose of this table, the specific gravities of various grades of polypropylene are assumed to be essentially equivalent. All of these formulations were designed to make corresponding plastic compounds that would yield a V-0 rating on a UL-94 flame test.[119] Underwriters Laboratory (UL) has established ignition-resistance classifications for plastics ranging from HB (least resistant) to V-0 (most resistant). UL-94 test protocol is a useful tool for screening flame retardants for plastic compounds in the early stages of formulation development. The test yields rudimentary data on the flammability of a material which can be used for comparing flame resistance of candidate flame retardants. Beyond that, there is no correlation of UL-94 test data with test results obtained using the UL 2335 or FM 4996 test protocols.[120] So once the preliminary candidacy of a flame retardant has

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[118] This subsection of the report was prepared for this report by James Innes & Ann Innes of Flame Retardants Associates.

[119] UL 94 is a small scale cone calorimeter used to evaluate the effect of flame retardants on flammability of a plastic. For more information on UL-94, see Appendix VIII.

[120] The fact that a small piece of plastic with a flame retardant compound meets even the highest-level UL-94 test level does not answer the question of what will happen to that same material in the dynamics of a large fire or in response to the water from a sprinkler system.

been established with UL-94 laboratory test data, the major work in testing, including preparation of enough material to make full size pallets for initial large scale fire tests, remains to be done.

Table 4.2: Polypropylene/Flame Retardant Compounds[121]

Flame Retardant Type	No Flame Retardant[122]	DecaBDE	Ammonium Polyphosphate System	Amino Phosphate/ proprietary amines	Magnesium Hydroxide
Polypropylene (PP)	100%	63%	63%	65%	45%
Flame Retardant		26%	37%	35%	65%
Antimony oxide		11%			
Total FR content	0%	37%	37%	35%	65%
Specific gravity	0.901	1.27	1.07	1.02	1.5

Table 4.2 shows that each of the flame retardants increases the specific gravity of the polypropylene compound. A PP compound made with decaBDE increases its specific gravity by 40%, ammonium polyphosphate by 18% and magnesium hydroxide by 66%. Therefore the cost of using less expensive flame retardants has to be tempered by the cost of using a greater weight of plastic compound to fill the mold. Both of the phosphate flame retardants have the lowest impact on specific gravity of the plastic compounds and they impart credible flame retardance. This information suggests phosphates should be considered as viable alternatives for decaBDE in plastic pallets.

For magnesium hydroxide, the level of flame retardant required in a polypropylene polymer to gain UL 2335 certification and/or FM 4996 approval, is somewhat less than 25%. To meet a similar requirement with a decaBDE compound requires a little over 10%. When the specific gravity and cost of each flame retardant is calculated using these lower required flame retardant levels, the cost per pound for each is similar, with

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[121] Data on all of the flame retardants was taken from the report by Sergei Levchik et al "Flame Retardants for Polypropylene," ICL Industrial Products.

[122] Data on polypropylene was taken from the report by Nicholas A. Zaksek of JJI Technologies "Innovative and Novel Non-Halogen Flame Retardants."

a slight advantage for the magnesium hydroxide compound. This suggests that magnesium hydroxide is also a viable alternative to decaBDE. To examine the complete analysis and calculations, see Appendix VI.

Chapter V: Alternative Non-Halogenated Flame Retardants

Previous chapters have reviewed the challenges of balancing flame retardancy, pallet performance characteristics and costs in bringing non-halogenated (NH) plastic pallets to market. But pallets with two different non-halogenated flame retardant systems are already on the market, and more may well be on the way with some companies in the process of planning FM or UL tests. Much of the information on current developments is proprietary, so we can't know for sure what alternatives are under development. Goals for the present study include bringing together non-proprietary information on alternative nonhalogenated flame retardants, and ensuring that the development of alternatives to decaBDE does not lead to unfortunate toxicological choices. This chapter will briefly bring together and review the information on potential non-halogenated flame retardants. The most promising of these have been selected for review under the Green Screen chemical toxicology assessment methodology developed by Clean Production Action. Chapter 6 will then present a description of the Green Screen methodology and a report on the results of the individual chemical assessments.

An Overview of Non-Halogen Flame Retardants in Plastic Pallets[123]

Fire resistant pallets have been successfully produced using one or more non-halogenated flame retardant chemicals and the pallets have been tested and certified by UL and FM as equivalent to wood. The issues with non-halogen flame retardants in plastic pallets, as discussed in the preceding chapters, relate primarily to cost and the adverse effects on physical properties that can occur when such flame retardant compounds are incorporated into a plastic matrix.

The following discussion of the potential for using nonhalogenated flame retardants as alternatives to decaBDE explains the strengths and weaknesses of the nonhalogenated flame retardants that: i) were identified as being feasible for use in polyolefins, the preferred plastic for making pallets; and ii) have been used successfully in plastic applications other than pallets.

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[123] Most of this section of Chapter V was prepared for this report by James Innes & Ann Innes of Flame Retardants Associates. The only exceptions are the second part of the subsection on magnesium hydroxide, and the subsections on melamine polyphosphate and melamine cyanurate.

Inorganic Metal Hydroxides

This is a class of flame retardants that is low in cost but requires high concentrations in plastic pallets to meet the criteria for UL 2335 and/or FM 4996. Therefore, the advantage of low unit cost is lost to the high concentrations of flame retardant.

$Mg(OH)_2$ (Magnesium Hydroxide)

Magnesium hydroxide is a compound that contains 31% chemically bound water. This water-insoluble compound, when dried and incorporated into a plastic polymer matrix, will form a composite. When exposed to fire, the composite first gives off chemically bound water (which cools the composite) at about 300 °C. After the water is released, a protective magnesium oxide (MgO) refractory layer is left behind which provides additional flame retardancy and an "anti-pooling" effect necessary in the idle pallet test. This flame retardant chemical is a heat absorbing type flame retardant. For a flame retardant plastic pallet application, the magnesium hydroxide would be incorporated into a polyolefin resin at about 23% loading.

In its powder form, magnesium hydroxide can be treated with particle treatment chemicals to improve its compatibility with the polymer matrix. The particle treatment chemicals include stearic acid and vinyl triethoxy silane. The particle treatment process allows for a better dispersion of the flame retardant in the polymer matrix and consequently better processability.

Rehrig Pacific has a patented, commercially available magnesium hydroxide-based flame retardant polypropylene plastic pallet. It incorporates about 23% magnesium hydroxide, in combination with aluminum trihydroxide and zinc borate, in a polypropylene polymer to pass the flammability requirements, and has a UL2335 listing.[124]

Aluminum trihydrate

Aluminum trihydrate (ATH) is also a compound with 34% chemically bound water. It works in the same fashion as magnesium hydroxide except that the water is released from ATH at a lower temperature, about 200 °C. This effectively limits its application to lower temperature polymers, and for plastic pallets that means ATH is suitable only for HDPE, not PP. Loading levels are the same as $Mg(OH)_2$ at about 23%. This one is also considered a heat absorbing type of flame retardant.

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[124] United States Patent: 7252041 "Flame retardant polyolefin pallets and flame retardant master batch for their production." Personal communication from Mike Lochner, Rehrig Pacific, November 19, 2010.

Major suppliers of ATH include Albemarle Corporation and Huber Engineered Materials with products under trade names such as Martinal®, Micral®, and Hymod®.

The authors are unaware of any idle pallet testing at either UL or FM on ATH-containing flame retardant plastic formulations.

Zinc Borate

Zinc borate (ZB) is an inorganic (no carbon) additive. When incorporated into the ATH or $Mg(OH)_2$ flame retardant systems, zinc borate produces an increased flame retardant effect. ZB is produced by reacting Borax (known to many via the 20 Mule Team brand) and zinc oxide. This is a powder product usually incorporated into the flame retardant system at 10-15% of the metal hydrate quantity used. When the composite is subjected to fire insult (exposure to fire according to test protocol) and the metal hydrate has formed the oxide, the ZB and that oxide combine to form a borate glass. This action increases the protection that the oxide layer provides. ZB is largely supplied by one company, US Borax, (Englewood, CO, owned by Rio Tinto) and marketed under the trade name Firebrake®. As with ATH, this technology modification is not known by the authors to have undergone idle pallet testing at either UL or FM.

Phosphates

Ammonium Polyphosphate

Ammonium polyphosphate (APP) is produced by the reaction of ammonium hydroxide and polyphosphoric acid to form an essentially insoluble ammonium phosphate. APP has been used as a flame retardant for polyolefins for over 30 years. In order to be effective as a polyolefin flame retardant, APP must be compounded with melamine and a product such as pentaerythritol, which acts as a carbon donor. The usual ratio of these components is 3:1:1. This product is typically compounded into the polyolefin at a concentration of about 12% to form a composite. When subjected to fire, the APP in the composite breaks down into a polyacid which chars the pentaerythritol. During the process, the melamine sublimes (goes directly from the solid to gas phase) causing the whole mass to intumesce. This intumescent (swollen) char insulates the remaining composite helping to mitigate additional heat insult from the fire. This flame retardant system effectively removes the fuel from the fire triangle picture and thus could be considered a char-forming type of flame retardant.

Suppliers include Budenheim (Spain), Clariant (Germany) and ICL (Israel, with USA operations in St. Louis, MO). Trade names for these producers’ APP products include respectively flame retardant CROS, Exolit®, and Phos-Chek P/30.

Ethylene diamine phosphate

Ethylene diamine combines with phosphoric acid to form ethylene diamine phosphate (EDAP). This compound has been offered as a flame retardant for polyolefin for over 20 years. Initially, it was offered by Albright & Wilson, later acquired by Rhodia. They discontinued their product, Amgard NP, and its manufacture was taken up by other producers. To be an effective flame retardant, EDAP is typically combined with melamine at a ratio of about 3 to 1. This product is incorporated into the polyolefin composite at about a 12% loading to meet the perceived required level for the idle pallet test. When subjected to fire insult, the EDAP decomposes first to phosphoric acid which then dehydrates (loses water) to a polyacid and, in the presence of pentaerythritol, produces char. During this process the melamine sublimes to provide intumescent action. This flame retardant is also considered a char former type of flame retardant.

Suppliers include JJI Technologies (Painesville, OH) and Unitex Chemical Corporation (Greensboro, NC). Trade names for EDAP from these companies are JJAZZ® and Uniplex® 44-94S.

Industry experts informed us that no formulations of the EDAP product or its combinations with melamine have been developed which meet UL or FM pallet standards. According to J. Day of Unitex,[125] the sell price of the blended system today is in the range of $2.00-$2.25/pound.

Melamine Polyphosphate

Melamine phosphates (MPP) are salts of melamine and phosphoric acid. These salts have good properties of thermal stability and are commonly used as flame retardants. Melamine and its derivatives (cyanurate and phosphates) are currently used in flexible polyurethane foams, intumescent coatings, polyamides, and thermoplastic polyurethanes. MPP meets the requirements for reporting for REACH[126] & RoHS.[127] When used with polyamides it is easy to process, eliminating the need for special

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[126] REACH (**R**egistration, **E**valuation, **A**uthorization and Restriction of **Ch**emical substances) is a European Community Regulation on chemicals and their safe use (EC 1907/2006). It became effective in 2007.

[127] RoHS (Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment Regulations) is a European Community regulation which first became effective in 2006. www.rohs.eu.

extruder screws. It has good heat stability with a decomposition temperature of 330°C.[128]

Melamine Cyanurate

Melamine cyanurate, is a salt of melamine and cyanuric acid. Melamine cyanurate has a higher thermal stability than pure melamine, with decomposition starting at 320 °C. Melamine cyanurate is often used as a flame retardant in polymers with higher melting temperatures, such as polyamides. Above 320°C, it undergoes endothermic decomposition to melamine and cyanuric acid, acting as a heat sink in the process. The vaporized melamine acts as an inert gas source diluting the oxygen and the fuel gases present at the point of combustion.

Due to the high decomposition temperature, melamine cyanurate is primarily used in engineering plastics such as nylon, polyphenylene oxide, and ABS. [129]

Melamine cyanurate is manufactured by ICL and U.S. Chemicals.

Phosphate Esters

Phosphate ester flame retardants include a group of chemical compounds which each has a different chemical structure. All are produced by the reaction of phosphorus oxychloride with an aromatic[130] organic compound. (Examples include trialkylated phenol phosphate or bisphenol A diphosphate.) In the flame retardant pallet application, the resin that is incorporated is not polyolefin, but MPPO (also known as Noryl®) which is a product made from modified polyphenylene oxide and high impact polystyrene (HIPS). Loading level ranges from 6-8%. When the MPPO is plasticized with the phosphate ester and is subjected to fire insult, the initial mechanism is a breakdown of phosphate ester into a polyacid which chars and protects the underlying substrate. There is a significant gas phase, radical-trapping mechanism occurring here, as well, with phosphorus aromatic compounds released during the pyrolysis (burning) process. So this type of flame retardant system can be considered a char-former type with a radical trapping mechanism as well.

Phosphate ester flame retardant products are supplied by Chemtura (Lafayette, IN), Daihachi Chemical Industry Company (Japan), and ICL Supresta (Dobbs Ferry, NY). Trade names include Reofos®, Kronitex®, CR733S, and Phosflex®.

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[128] Information on melamine polyphosphate was supplied by ToxServices (see Appendix IX)

[129] Information on melamine cyanurate was supplied by ICL corp.

[130] Aromatic compounds are organic compounds that have a ring structure with resonating double bonds that makes them extremely stable. The most common example is benzene.

Selection of Alternatives to Review

The effectiveness and relatively low cost of using decaBDE as a flame retardant in plastic pallets has served, in the past, as a disincentive to development of plastic pallets using nonhalogenated alternative flame retardants. But the combination of state restrictions on decaBDE and US EPA's voluntary agreement with manufacturers to bring sales of decaBDE to an end dramatically shifts those incentives. The previous chapters have explored both the technical and cost challenges of developing new alternatives. In a highly competitive market dominated by a low cost alternative, overcoming these barriers is difficult. It is reasonable to ask whether design, development and flame retardancy testing costs can be recovered, or whether the market would accept the higher price of an alternative non-halogenated flame retardant plastic pallet. Maine's new restrictions on the use of halogenated flame retardants in pallets has not eradicated those constraints, but probably alleviates them. They also provide a market opportunity for the pallet manufacturer with the best answer to the puzzle. While too much of the information is proprietary to be sure what new flame retardants may be coming to market, it seems probable that new flame retardant compounds with non-halogenated alternatives will be emerging.[131]

While there is no way to be certain which alternatives have greatest promise or are currently being developed or tested, we have used the information from the many sources presented in this and previous chapters to select some that seem the most promising (Table 5.1) for toxicological review with the Green Screen methodology. The results of the assessments of these non-halogenated flame retardants, along with a comparative assessment of decaBDE, are presented in the next chapter.

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[131] As noted in Table 2.4, there are currently two pallets with non-halogenated alternatives that have passed the UL 2335 or FM 4996 tests, one of which is on the market and the other of which just began production in December 2010. Comparisons with a decaBDE flame retardant pallet can be found in Chapter VII.

Table 5-1: Non-Halogenated Flame Retardants Selected for Review with Green Screen

Flame Retardant	CAS#	Reason for Selection
Melamine polyphosphate	218768-84-4	Recommended by PINFA[132].
Ethylenediamine phosphate	14852-17-6	Demonstrated FR properties for polypropylene
Ammonium polyphosphate	68333-79-9	Excellent general purpose FR but recommended for use with synergists
Red phosphorus	7723-14-0	Demonstrated application in thermoplastics
Magnesium hydroxide	1309-42-8	Demonstrated FR properties in thermoplastics and is currently being used in a polypropylene pallet
Aluminum trihydroxide	21645-51-2	Demonstrated FR properties in PE but not in PP
Zinc Borate	138265-88-0	Useful as a supplemental FR with ATH and Magnesium Hydroxide
Magnesium stearate	557-04-0	Magnesium hydroxide particles treated with stearate acid to facilitate a better dispersion of magnesium hydroxide in a polymer matrix

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[132] Phosphorus, Inorganic and Nitrogen Flame Retardants Association

Chapter VI: Flame Retardant Toxicity Assessments[133]

This chapter evaluates health and environmental hazards and assigns Green Screen hazard ratings to the flame retardant decabromodiphenyl ether (decaBDE) and eight alternate flame retardants using Clean Production Action's (CPA) Green Screen (Version 1.0) [134][135]. For each flame retardant, endpoints relating to human health effects, aquatic toxicity, and environmental effects were evaluated, and each endpoint was assigned a score of Low hazard (L), Moderate hazard (M), High hazard (H), or very High hazard (vH).

CPA's Green Screen is an Alternatives Assessment tool developed to assist the industry in selecting safer chemical alternatives. Alternatives Assessment is an approach used to assess a chemical's impact on human health and the environment. The goal is to find a science-based solution that identifies hazards, and as a result, promotes the selection of less hazardous chemical ingredients.

The following are procedures used by Green Screen in an Alternatives Assessment:

- To determine the need for and potential benefits of an alternatives assessment, the reviewer considers whether alternatives are commercially available and cost effective; whether alternatives have the potential for an improved health and environmental profile; and whether they are likely to result in lasting change.
- Through literature review and discussion with stakeholders, information is collected about viability on a range of potential alternatives. The focus is on finding alternatives. The reviewer may also include viability demonstrations by chemical and product manufacturers.
- Based on the best data that are available from the literature or that can be modeled, a hazard concern level is assigned (High, Moderate or Low) for each alternative across a range of endpoints including: acute and repeated dose toxicity; carcinogenicity and mutagenicity; reproductive and developmental toxicity; neurotoxicity; sensitization and irritation; acute and chronic aquatic toxicity; persistence; and bioaccumulation. In addition, a qualitative description of potential endocrine activity may be assigned.

Sources of information for a hazard assessment include one or more of the following:

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[133] This Chapter prepared by scientific consulting firm ToxServices.

[134] Clean Production Action (CPA). The Green Screen for Safer Chemicals, Version 1. September, 2009.

[135] CPA recommends independent third-party validation of all Green Screen assessments. No independent third-party validation has been done for this report. Companies may not make marketing claims based on a Green Screen assessment that has not undergone an independent validation.

- Publicly available measured (experimental) data obtained from a literature review;
- Measured data contained in confidential business information received by EPA;
- Structure-Activity-Relationship- (SAR) based estimations from EPA's Pollution Prevention Framework and Sustainable Futures predictive methods;
- Confidential data in experimental studies supplied by the chemical manufacturers.

When measured data are not available or adequate for an endpoint, a hazard concern level can be assigned based on SAR and expert judgment. This practice ensures that all endpoints are considered as part of the hazard assessment and that alternatives are evaluated based on as complete an understanding of their human health and environmental characteristics as possible. A level of confidence associated with hazard assignments is assigned.

Once the hazard assessment is complete, an Alternatives Assessment report is written to provide contextual and supplemental information designed to aid in decision-making and may include descriptions of manufacturing processes, use patterns, and life-cycle stages that may pose special exposure concerns.

Green Screen Screening Methods

The Green Screen is a comparative hazard assessment tool that manages chemical risk by reducing hazards rather than controlling exposure to potentially toxic chemicals. [136] Hazard assessment is the process of determining whether exposure to an agent can cause an increase in the incidence of adverse health effects (such as an allergic reaction, birth defect, or cancer), and involves a characterization of the nature and strength of the evidence of causation[137] . A comparative hazard assessment evaluates hazards from two or more agents, with the intent to guide decision making toward the use of the least hazardous options via a process of informed substitution.

In practical terms, comparative hazard assessment is a term that describes the practice of assessing hazards for specific items (such as chemicals or technologies), and then comparing these hazards following a structured approach. Ideally, comparative hazard assessment minimizes subjectivity in hazard classification since a structured approach is

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[136] Clean Production Action. 2010. Clean Production Action's Green Screen. http://www.cleanproduction.org/Greenscreen.php

[137] Kofi Asante-Duah, D. 1993. Risk assessment techniques and methods of approach. In Hazardous Waste Risk Assessment. Chelsea: Lewis Publishers, pp.59-158.

used to assign hazards, allowing decision makers to optimize health and environmental benefits.

The Green Screen for Safer Chemicals is a quantitative chemical screening method designed to help manufacturers identify inherently less hazardous chemicals using a standardized approach that considers both human health and environmental effects. As part of a Green Screen evaluation process, each ingredient or chemical is assigned a Concern Level. Individual hazards are evaluated for almost one dozen hazard endpoints (such as carcinogenicity, reproductive toxicity, neurotoxicity, aquatic toxicity, persistence, and bioaccumulation) and then a hazard rating of very High, High, Moderate, or Low is assigned for each endpoint for each chemical. The Concern Levels are then collectively evaluated in Green Screen Version 1.0 to one of four different benchmark scores, as illustrated below in Figure 1:[138]

- Benchmark One: Avoid (Chemical of High Concern)
- Benchmark Two: Use (But Search for Safer Substitutes)
- Benchmark Three: Use (But Still Opportunity for Improvement)
- Benchmark Four: Prefer (Safer Chemical).

For each flame retardant evaluated in this report, endpoints relating to human health effects, aquatic toxicity, and environmental effects were evaluated following the criteria established in Green Screen Version 1.0.[139] As noted above, the Green Screen identifies the following health effects: acute toxicity; corrosion/irritation; sensitization; systemic toxicity; carcinogenicity; mutagenicity; reproductive/developmental toxicity; endocrine disruption; or neurotoxicity.

Authoritative lists specified in CPA's Hazard Threshold Table (dated 11/01/2009) were searched for each chemical listed,[140] as was the CPA Red list of chemicals dated May 13, 2009.[141]

In instances where a large data gap exists for a chemical (either for a health effect or environmental effects endpoint), one or more structurally similar surrogates are analyzed for that particular endpoint. This approach is based on the assumption that a chemical's structure imparts properties that relate to biological activity, and that a group of chemicals that produce the same activity have something similar about their

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[138] Clean Production Action. 2010. Clean Production Action's Green Screen. http://www.cleanproduction.org/Greenscreen.php

[139] Clean Production Action (CPA). The Green Screen for Safer Chemicals, Version 1. September, 2009.

[140] Clean Production Action (CPA). Green Screen Hazard Threshold Table, Version 1. November 3, 2009.

[141] Clean Production Action (CPA). Red list of chemicals. May 13, 2009.

chemistry and/or structure.[142] Chemicals produced by similar methods by the same company and used for similar purposes make good potential analogs. In addition, degradation products of the parent compound can be used as surrogates especially if the parent compound is expected to break down readily in the environment. The Organization of Economic Co-operation and Development (OECD)[143] and U.S. Environmental Protection Agency (U.S. EPA)[144] have defined guidelines for identifying similar substances to use analogs based on the following commonalities:

- A common functional group or substance (e.g. phenols, aldehydes);
- A common precursor or break-down product may result in structurally similar chemicals, which can be used to examine related chemicals such as acids/esters/salts (e.g. short-chained alkyl-methacrylate esters which are metabolized to methacrylic acid);
- An incremental or constant change (e.g. increased carbon chain length; typically used for physiochemical properties such as boiling point); and
- Common constituents or chemical class, similar carbon range numbers (used with substances of unknown or variable composition), complex reaction products or biological material.

CPA's Green Screen Version 1.0 was initially developed to assess only organic chemicals. Because most inorganic chemicals contain covalent bonds, they do not break down readily and are likely to persist in the environment for longer periods of time. Persistence alone does not indicate a chemical is hazardous. Chemicals that are persistent as well as bioaccumulative and toxic are of high concern as their concentrations in the environment increase over time, allowing for more opportunity to exert a toxic effect on human health. Version 1.0 criteria states that a score of High for persistence results in an automatic Benchmark score of 2 (Use but Search for Safer Substitutes). Version 2.0 will be expanded to address inorganics such as mineral oxides

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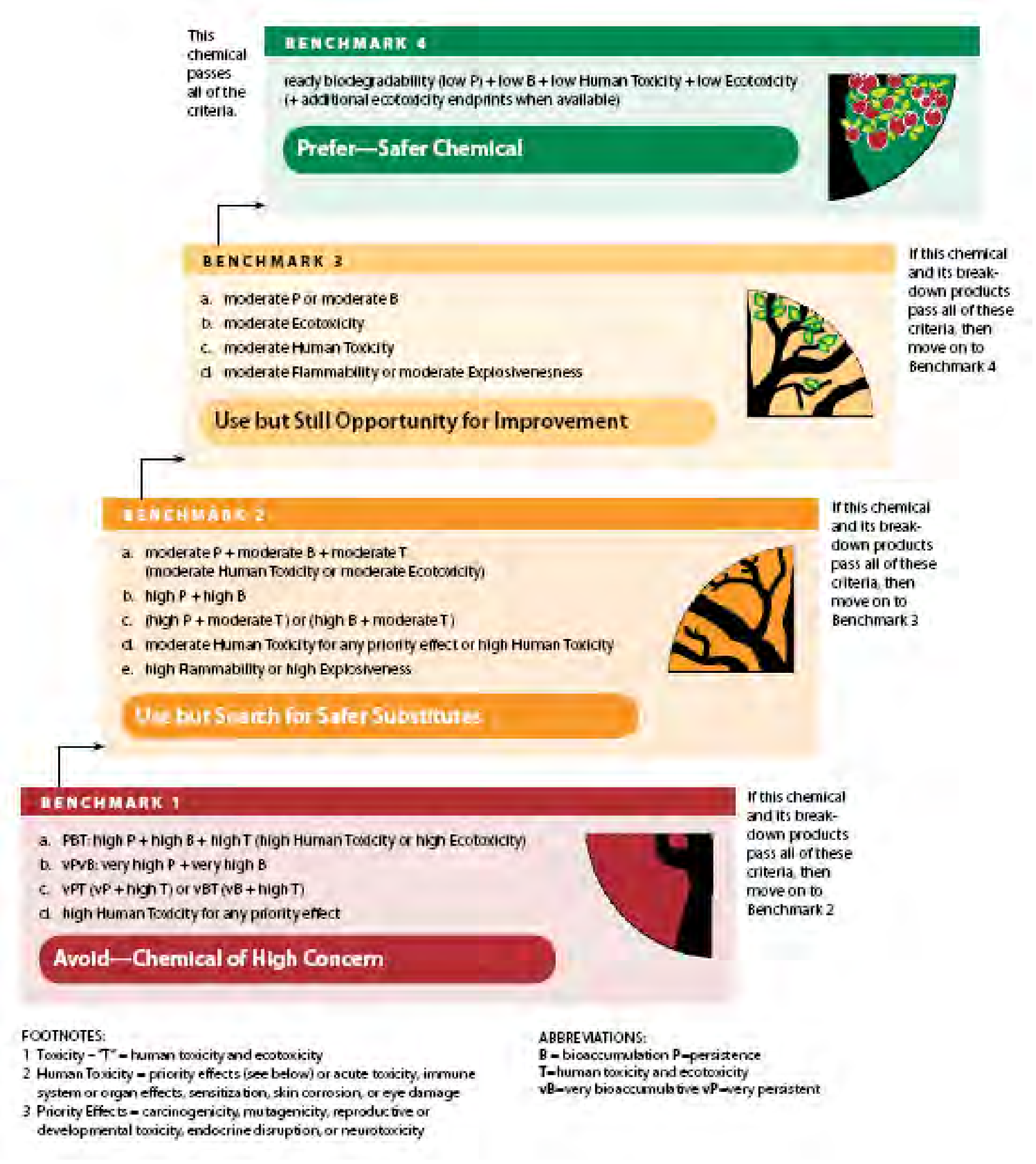
[142] United States Environmental Protection Agency (U.S. EPA). 2010. Predicting the Toxicities of Chemicals to Aquatic Animals Species. http://water.epa.gov/scitech/swguidance/waterquality/standards/criteria/aqlife/upload/whitepaper_effects.pdf.

[143] Under the guidelines published by Organisation for Economic Co-operation and Development (OECD), an analog selected to fill a data gap must be data rich and share similar physical and chemical properties, including behavior in physical or biological process, with the original compound. Organisation for Economic Co-operation and Development (OECD). 2007. Guidance on Grouping of Chemicals. OECD Environment Health and Safety Publications. Series on Testing and Assessment No. 80.

[144] U.S. EPA. 2010. Predicting the Toxicities of Chemicals to Aquatic Animals Species. http://water.epa.gov/scitech/swguidance/waterquality/standards/criteria/aqlife/upload/whitepaper_effects.pdf

to allow for comparison of inorganic chemicals used as flame retardants. Under Version 2.0 criteria, an inorganic chemical with a Low hazard rating for human and ecotoxicity across all hazard endpoints and a Low hazard rating for bioaccumulation and persistence will not be deemed problematic. Inorganic chemicals that are only persistent will be evaluated under the criteria for Benchmark 4.

Figure 6.1: CPA Green Screen Benchmark Scores (CPA 2009a)



This chemical passes all of the criteria.

BENCHMARK 4

ready biodegradability (low P) + low B + low Human Toxicity + low Ecotoxicity
(+ additional ecotoxicity endprints when available)

Prefer—Safer Chemical

If this chemical and its break-down products pass all of these criteria, then move on to Benchmark 4

BENCHMARK 3

a. moderate P or moderate B
b. moderate Ecotoxicity
c. moderate Human Toxicity
d. moderate Flammability or moderate Explosivenesness

Use but Still Opportunity for Improvement

If this chemical and its break-down products pass all of these criteria, then move on to Benchmark 3

BENCHMARK 2

a. moderate P + moderate B + moderate T
(moderate Human Toxicity or moderate Ecotoxicity)
b. high P + high B
c. (high P + moderate T) or (high B + moderate T)
d. moderate Human Toxicity for any priority effect or high Human Toxicity
e. high Flammability or high Explosiveness

Use but Search for Safer Substitutes

If this chemical and its break-down products pass all of these criteria, then move on to Benchmark 2

BENCHMARK 1

a. PBT: high P + high B + high T (high Human Toxicity or high Ecotoxicity)
b. vPvB: very high P + very high B
c. vPT (vP + high T) or vBT (vB + high T)
d. high Human Toxicity for any priority effect

Avoid—Chemical of High Concern

FOOTNOTES:
1 Toxicity – "T" = human toxicity and ecotoxicity
2 Human Toxicity = priority effects (see below) or acute toxicity, immune system or organ effects, sensitization, skin corrosion, or eye damage
3 Priority Effects = carcinogenicity, mutagenicity, reproductive or developmental toxicity, endocrine disruption, or neurotoxicity

ABBREVIATIONS:
B = bioaccumulation P=persistence
T=human toxicity and ecotoxicity
vB=very bioaccumulative vP=very persistent

Overview of Chemicals Profiled

This report evaluates health and environmental hazards posed by decaBDE, as well as hazards posed by eight alternative flame retardants: aluminum trihydroxide, ammonium polyphosphate, ethylenediamine phosphate, magnesium hydroxide, magnesium stearate, melamine polyphosphate, red phosphorus, and zinc borate.

Chemical flame retardants are added to many day-to-day products to prevent or suppress ignition of a fire or to limit the spread of fire once ignition has occurred. Flame retardants can be categorized into two main groups: additive or reactive.[145] The majority of flame retardants are of the additive type which can be added to a manufactured product without being chemically bound to it. This makes them less effective than reactive flame retardants which are incorporated into the final product during manufacturing. Flame-retardant synergists are an additional category of chemicals that do not have significant flame-retarding properties by themselves; however, their use increases the overall effectiveness of a flame-retardant system.

Additive flame retardants can be further classified as either halogenated (compounds containing chlorine or bromine bonded to carbon) or non-halogenated. Ongoing research into less toxic flame retardants is focused on non-halogen alternatives which are less likely to persist in the environment and to bioaccumulate in organisms. They also have the benefit of degrading more readily, reducing their potential long-term impact on human health and the environment.[146]

DecaBDE is a member of the structurally similar subset of brominated flame retardants called polybrominated diphenyl ethers (PBDEs). In PBDEs, there are ten possible sites for bromine to bind to the diphenyl ether backbone; decaBDE represents the full saturation of the molecule, meaning all ten sites are populated with a bromine atom. PBDEs are used as flame retardants in a variety of products including building materials, electronics, furnishings, polyurethane foams, and textiles.

Commercial decaBDE generally has a purity of 97%; common impurities include lower brominated diphenyl ethers such as nonabromodiphenyl ethers and octabromodiphenyl

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[145] United States Environmental Protection Agency (U.S. EPA). 2005. Furniture Flame Retardancy Partnership: Environmental Profiles of Chemical Flame-Retardant Alternatives for Low-Density Polyurethane Foam. Volume 1. Design for the Environment (DfE). http://www.epa.gov/dfe/pubs/flameret/altrep-v1/altrepv1-f1c.pdf

[146] Department of Ecology (DOE). 2008. Alternatives to DecaBDE in Televisions and Computers and Residential Upholstered Furniture. Washington State Department of Health Publication No. 334-181.

ethers. The lesser brominated PBDEs (i.e., those with fewer bromine atoms per molecule, such as the pentaBDE and octaBDE formulations that already have been removed from the market), are considered more toxic than the more brominated PBDEs (such as decaBDE), because lesser brominated PBDEs are more likely to bioaccumulate. Although decaBDE is a higher brominated PBDE, it is known to degrade into lower brominated diphenyl ethers readily via light and microorganisms making decaBDE a cause for concern for the flame retardant industry.[147]

According to the Illinois Environmental Protection Agency (IEPA), PBDEs are being detected in soil, water, sediment, air, and animals and humans worldwide in increasing concentrations.[148] One study in particular showed a significant increase of decaBDE concentrations in peregrine falcon eggs from the northeastern U.S.[149] The most sensitive human health effects of PBDEs include liver, thyroid, reproductive/ developmental, and neurological effects.[150] Currently, industry is in the process of phasing out the use of PBDEs as flame retardants due to adverse human and environmental health effects of the chemicals. Initially, legislation focused on the phase-out of penta- and octa- BDE; however, more initiatives are looking into alternatives to decaBDE as well.[151] The sole U.S. manufacturer of pentaBDE voluntarily agreed to halt production following the European Union's (EU) ban of the chemical in 2004[152]. Since then, laws in 13 states including California, Connecticut, Hawaii, Illinois, Maine, Maryland, Massachusetts, Michigan, Minnesota, New York, Oregon, Rhode Island, and Washington have enacted or introduced legislation relating to PBDEs.[153]

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[147] Illinois Environmental Protection Agency (IEPA). 2007. Report on Alternatives to the Flame Retardant DecaBDE: Evaluation of Toxicity, Availability, Affordability, and Fire Safety Issues. A Report to the Governor and the General Assembly.

[148] Ibid.

[149] Chen, D., M.J. La Guardia, and E. Harvey. 2008. Polybrominated Diphenyl Ethers in Peregrine Falcon (*Falco peregrines*) Eggs from the Northeastern U.S. Environ. Sci. Technol. 42(20); 7594-7600. As described in: Department of Ecology (DOE). 2008. Alternatives to DecaBDE in Televisions and Computers and Residential Upholstered Furniture. Washington State Department of Health Publication No. 334-181.

[150] Illinois Environmental Protection Agency (IEPA). 2007. Report on Alternatives to the Flame Retardant DecaBDE: Evaluation of Toxicity, Availability, Affordability, and Fire Safety Issues. A Report to the Governor and the General Assembly.

[151] Ibid.

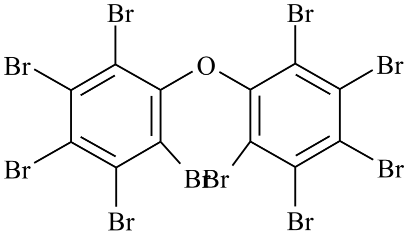
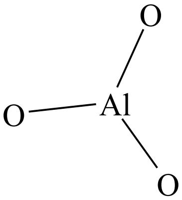
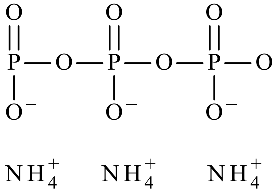
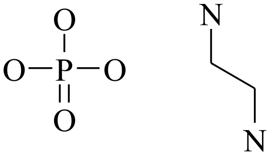
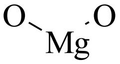
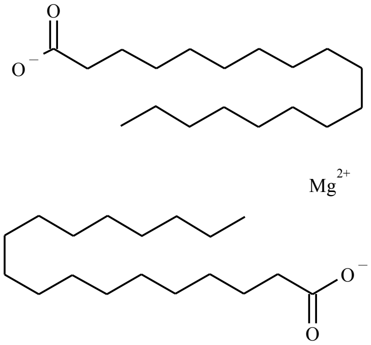
[152] United States Environmental Protection Agency (U.S. EPA). 2005. Furniture Flame Retardancy Partnership: Environmental Profiles of Chemical Flame-Retardant Alternatives for Low-Density Polyurethane Foam. Volume 1. Design for the Environment (DfE). Available: http://www.epa.gov/dfe/pubs/flameret/altrep-v1/altrepv1-f1c.pdf

[153] Illinois Environmental Protection Agency (IEPA). 2007. Report on Alternatives to the Flame Retardant DecaBDE: Evaluation of Toxicity, Availability, Affordability, and Fire Safety Issues. A Report to the Governor and the General Assembly.

Washington, Maine, and Oregon have all proposed statutes restricting the use of decaBDE by January 1, 2010.

The nine flame retardants are illustrated in Table 6.2 and are briefly described below.

Table 6.1: Nine Flame Retardant Chemicals Evaluated Using Green Screen

Chemical Name	CAS #[154]	Structure	Type of Flame Retardant
Decabromodiphenyl ether (decaBDE)	1163-19-5		Brominated additive (halogenated)
Aluminum trihydroxide	21645-51-2		Mineral-based additive (non-halogenated)
Ammonium polyphosphate	68333-79-9		Phosphorus-based additive (non-halogenated)
Ethylenediamine phosphate	14852-17-6		Phosphorus-based additive (non-halogenated)
Magnesium hydroxide	1309-42-8		Mineral-based additive (non-halogenated)
Magnesium stearate	577-04-0		Mineral-based additive (non-halogenated)

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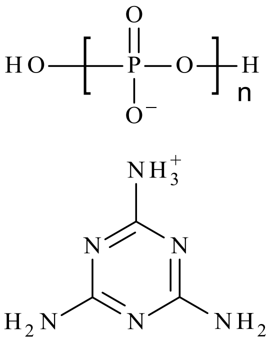
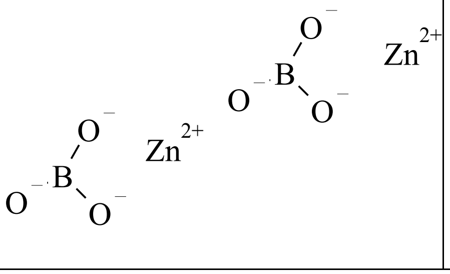
[154] CAS Registry Numbers are unique numbers given to chemicals by the Chemical Abstracts Service.

Melamine polyphosphate	218768-84-4		Nitrogen-based additive (non-halogenated)
Red phosphorus	7723-14-0	$P^{(0)}$	Mineral-based additive (non-halogenated)
Zinc borate	1332-07-6		Synergist in non-halogenated and halogenated systems

Aluminum trihydroxide is a solid, non-halogenated flame retardant. It is also used in the manufacturing of glass, ceramics, activated alumina, and mattress bedding. Aluminum trihydroxide is an additive mineral flame retardant, filler, and an additive for fume reduction. Because it is a relatively weak-acting flame retardant, it must be utilized in large quantities, which limits its application area. In addition, aluminum trihydroxide decomposes at 200˚C, which further limits its application and it cannot be used in plastics with high processing temperatures.

Ammonium polyphosphate (APP) is a solid, ionic, non-volatile polymer used for flame retardation. APP is an intumescent coating, meaning it swells as a result of heat exposure and produces a carbonaceous foam which is a poor conductor of heat, thus retarding heat transfer. APP has excellent flame retardant characteristics in cellulose-containing materials such as paper and wood products but is also classified for use on steel and plastic surfaces as well as adhesives and sealants. Additionally, APP is also used as a fertilizer. Because no relevant toxicity data were identified for the possible reproductive, developmental, acute and systemic toxicity of APP, sodium tripolyphosphate, was selected as a chemical surrogate due to its structural similarity, use as a flame retardant, and use as a surrogate in several previous reports.

Ethylenediamine phosphate is a non-halogenated flame retardant salt composed of a mixture of ethylenediamine and phosphate. Because no relevant toxicity data were identified to assess possible skin/eye corrosion, skin/respiratory sensitization, mutagenicity, reproductive, developmental, acute, or systemic toxicity of ethylenediamine phosphate, the individual components, ethylenediamine and phosphate, were evaluated to address data gaps.

Magnesium hydroxide is commonly used as an antacid and is the active ingredient in the laxative milk of magnesia. Additionally, it is used as a residual fuel-oil additive, an alkali drying agent in food, a color-retention agent, and is an ingredient in teeth. Magnesium hydroxide is used as a flame retardant in commercial furniture applications in the United States in addition to commercial and residential furniture in the United Kingdom. The stability of magnesium hydroxide at temperatures above 300°C allows it to be incorporated into several polymers.

Magnesium stearate is commonly used as a binder in drug tablets and as an emulsifier in cosmetics. Magnesium stearate is Generally Recognized as Safe (GRAS)[155] for addition to food; therefore the chemical is not thought to pose serious health hazards to humans at low levels of exposure. Environmentally however, the chemical has a tendency to persist.

Melamine phosphates are salts of melamine and phosphoric acid. These salts have good properties of thermal stability and are commonly used as flame retardants. Melamine and its derivatives (cyanurate and phosphates) are currently used in flexible polyurethane foams, polyamides and thermoplastic polyurethanes, and flame retardant (intumescent) coatings. There were not extensive data for melamine polyphosphate. In cases of data gaps, data for melamine phosphate, and the ions for melamine and phosphate were considered.

Red phosphorus is one of three allotropic forms[156] of the element phosphorus. Black phosphorus is the least reactive allotrope and is produced by heating white phosphorus under high pressure (about 12,000 atmospheres). White phosphorus, sometimes called

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[155] Food and Drug Administration (FDA) guidance on GRAS states: "'GRAS' is an acronym for the phrase **G**enerally **R**ecognized **A**s **S**afe. Under sections 201(s) and 409 of the Federal Food, Drug, and Cosmetic Act …, any substance that is intentionally added to food is a food additive, that is subject to premarket review and approval by FDA, unless the substance is generally recognized, among qualified experts, as having been adequately shown to be safe under the conditions of its intended use, or unless the use of the substance is otherwise excluded from the definition of a food additive." http://www.fda.gov/Food/GuidanceComplianceRegulatoryInformation/GuidanceDocuments/FoodIngredientsandPackaging/ucm061846.htm#Q1.

[156] Phosphorus is among the chemical elements that exhibit "allotropy," the property to exist in two or more different forms or "allotropes." See *Wikipedia*, http://en.wikipedia.org/wiki/Allotropy.

yellow phosphorus, is the least stable, most reactive, most volatile, and most toxic of the three isotopes. Exposure to sunlight can cause white phosphorus to convert into amorphous red phosphorus. Further heating results in the amorphous red phosphorus becoming crystalline. Red phosphorus can be converted back to white phosphorus by heating it to 260˚C.

Zinc borate is used as a flame retardant in conjunction with other chemicals, including antimony trioxide, magnesium hydroxide, alumina trihydrate, and some brominated flame retardants. There are limited studies in the literature characterizing the toxicity of zinc borate. However, multiple toxicity studies have been performed on other inorganic borates. Additionally, zinc borate readily breaks down in the stomach to zinc oxide (ZnO) and boric acid (H_3BO_3). Therefore, in the absence of data for zinc borate, data for zinc oxide and boric acid have been substituted.

Results

Table 6.3 summarizes the hazard ratings and provides the Green Screen Benchmark scores for the nine flame retardants. These ranged from 1 to 4: one chemical received a Green Screen score of 4 ("Prefer- Safer Chemical"); six chemicals received Green Screen scores of 2 ("Use but Search for Safer Substitutes"); and two chemicals, including decaBDE, received Green Screen scores of 1 ("Avoid-Chemical of High Concern").

Only ammonium polyphosphate received a Green Screen score of 4 ("Safer Chemical") because no concerns regarding human health effects, aquatic toxicity, or environmental effects were identified.

Six chemicals received Green Screen (GS) scores of 2 ("Use but Search for Safer Substitutes"):

- ***Aluminum trihydroxide:*** GS 2 score due to its moderate neurotoxicity, irritation, repeat dose toxicity and very High persistence.
- ***Ethylenediamine phosphate:*** GS 2 score due to its moderate mutagenicity, reproductive/developmental toxicity, acute toxicity and repeat dose toxicity. Ethylenediamine phosphate also received High hazard rankings due to potential irritation, sensitization, and chronic aquatic toxicity.
- ***Magnesium hydroxide:*** GS 2 score due to its moderate irritation and repeat dose toxicity, as well as its very high persistence.
- ***Magnesium stearate***: GS 2 score due to its high persistence and moderate irritation/corrosion and systemic toxicity.

- ***Melamine polyphosphate:*** GS 2 score due to its moderate carcinogenicity, mutagenicity, and persistence, in addition to its high repeat dose toxicity.
- ***Zinc borate***: GS 2 score based on its very high persistence and moderate reproductive and developmental toxicity as well as acute aquatic toxicity.

In addition to the Green Screen score of 1 assigned to decaBDE, red phosphorus was also assigned a Green Screen score of 1 (“Avoid-Chemical of High Concern”).

- ***Red phosphorus:*** GS 1 score for hazard ratings of high for neurotoxicity, acute toxicity, irritation, and repeat dose toxicity. In addition, red phosphorus received hazard ratings of high for explosivity and flammability. Based on the high scores for neurotoxicity, acute toxicity, irritation, and repeat dose toxicity, and red phosphorus’s conversion into the more toxic white phosphorus via exposure to sun light, red phosphorus was assigned a benchmark score of 1.
- ***DecaBDE***: GS 1 score based on its special risk due to its affinity to persist and bioaccumulate in the environment where it can enter the food chain and eventually pose a toxic risk to humans. This is significant because chemicals with moderate to high human toxicity that persist in the environment are able to exert their toxic effects over a long period of time.

Table 6.2: Green Screen (Version 1.0) Levels of Concern for Nine Flame Retardants

Screening Level Toxicology Hazard Summary

Chemical	CAS #	Human Health Effects									Aquatic Toxicity		Fate		Physical		GS Benchmark Score (Chemical)
		Carcinogenicity	Mutagenicity	Reproductive/ Developmental	Endocrine Disruption	Neurotoxicity	Acute Toxicity	Skin/Eye Corrosion/Irritation	Dermal/Respiratory Sensitization	Systemic Toxicity/ Repeated Dose	Acute Aquatic	Chronic Aquatic	Persistence	Bioaccumulation	Explosivity	Flammability	
Decabromodiphenyl Ether	1163-19-5	**M**	**L**	**M**	**M**	**M**	**L**	**M**	**L**	**M**	**H**	**H**	**vH**	**M**	nd	**L**	1
Aluminum Trihydroxide	21645-51-2	**L**	*L*	**L**	nd	**M**	**L**	**M**	**L**	**M**	**L**	*M*	**vH**	**L**	**L**	**L**	2
Ammonium Polyphosphate	68333-79-9	**L**	**L**	*L*	nd	nd	**L**	**L**	**L**	*L*	**L**	*L*	**L**	**L**	**L**	**L**	4
Ethylenediamine Phosphate	14852-17-6	**L**	*M*	*M*	nd	nd	*M*	*H*	*H*	*M*	**L**	**H**	**M**	**L**	**L**	**L**	2
Magnesium Hydroxide	1309-42-8	**L**	**L**	**L**	nd	*L*	**L**	**M**	*L*	**M**	**L**	**L**	**vH**	**L**	**L**	**L**	2
Magnesium Stearate	557-04-0	**L**	**L**	**L**	nd	nd	**L**	**M**	**L**	**M**	*L*	*M*	**H**	**L**	**M**	**H**	2
Melamine Polyphosphate	218768-84-4	*M*	*M*	**L**	nd	nd	**L**	**L**	*L*	*H*	*L*	*L*	*M*	**L**	**L**	**L**	2
Red Phosphorus	7723-14-0	**L**	**L**	**L**	nd	**H**	**H**	**H**	**L**	**H**	**L**	**M**	**M**	**L**	**H**	**H**	1
Zinc Borate	1332-07-6	**L**	**L**	*M*	*M*	nd	**L**	**M**	**L**	**M**	**H**	nd	nd	**L**	**L**	**L**	2

nd=not determined/unknown
L=Low Hazard **M**=Moderate Hazard **H**=High Hazard **vH**=very High Hazard-Endpoints in colored text (**L, M, and H**) were assigned based on experimental data.
Endpoints in black italics (*L*, *M*, and *H*) were assigned using estimated values and professional judgment (Structure Activity Relationships)

Comparative Hazard Assessment

As presented in Table 3, Green Screen scores assigned for the nine flame retardants demonstrate that other than red phosphorus, several less hazardous alternatives for decaBDE exist. Among the eight alternative flame retardants screened, ammonium polyphosphate (APP) has been shown to have acceptable health effects and environmental toxicity profiles, and is not likely to persist in the environment. This favorable profile resulted in APP receiving a Green Screen score of 4, which is the most favorable Green Screen rating among all eight alternative flame retardants screened.

Six of the alternative flame retardants received Green Screen scores of 2, indicating that they are less hazardous than decaBDE. These chemicals are: aluminum trihydroxide, ethylenediamine phosphate, magnesium hydroxide, magnesium stearate, melamine polyphosphate, and zinc borate. Two of these chemicals, aluminum trihydroxide and magnesium hydroxide, were assigned final Benchmark scores of 2 based on very high persistence. Both chemicals are fully oxidized inorganic materials, and are therefore not expected to biodegrade, oxidize in air, or undergo hydrolysis or pyrolysis under normal environmental conditions. In fact, no degradation processes under typical environmental conditions were identified (U.S. EPA 2008). Under the CPA's Version 1.0 criteria, "recalcitrant" chemicals (chemicals that are resistant to degradation), although not inherently toxic, are assigned a Benchmark score of 2. Both of these chemicals were assigned a low mark for bioaccumulation, making them less of a risk to the environment because they are not expected to accumulate in aquatic and terrestrial organisms.

Ethylenediamine phosphate, magnesium stearate, melamine polyphosphate, and zinc borate all received final Benchmark scores of 2 after receiving scores of high for one or more toxicity endpoints. A score of high for any endpoint will result in a chemical receiving a final Benchmark score of 2.

Conclusion

This report evaluates the health and environmental hazards of nine different flame retardants. Each chemical was evaluated against the health and environmental fate and toxicity criteria of Clean Production Action's Green Screen, Version 1.0.[157] For each flame retardant, endpoints relating to human health effects, aquatic toxicity, and environmental effects were evaluated,

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[157] Clean Production Action (CPA). 2009. The Green Screen for Safer Chemicals, Version 1. September, 2009.

and each endpoint was given a score of Low hazard (L), Moderate hazard (M), High hazard (H), or very High hazard (vH).

The Green Screen is a hazard-based screening tool and its predicted results should be considered as such. Hazard assessments are components of a risk assessment, but do not in themselves constitute a risk assessment.[158] In most industries, hazards cannot be abolished in the sense that they are completely removed. The Green Screen is a valuable tool in that it can be used for both informed substitution and continuous improvement of formulated materials through use of less hazardous ingredients.

Green Screen scores assigned for the nine flame retardants demonstrated that other than red phosphorus, several alternatives for decaBDE exist. Namely, ammonium polyphosphate has been shown to have low human and environmental toxicity and is unlikely to persist in the environment, and received a Green Screen score of 4 (“Safer Chemical”), while six chemicals received Green Screen scores of 2 (“Use but Search for Safer Substitutes”).

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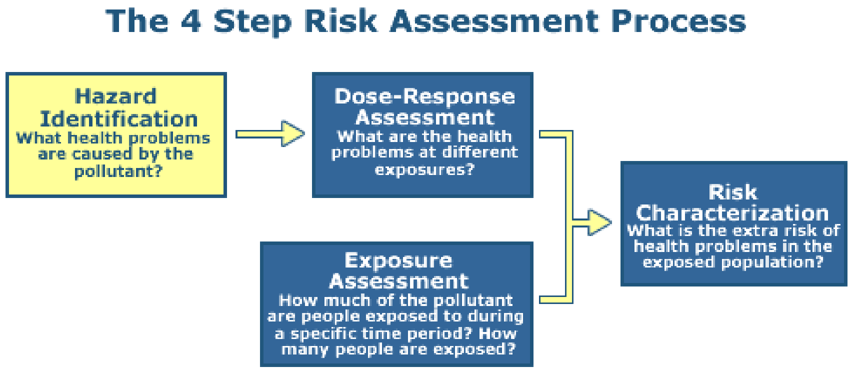
[158] National Research Council Committee to Review the OMB Risk Assessment Bulletin (NRC), 2007. Scientific Review of the Proposed Risk Assessment Bulletin from the Office of Management and Budget. The National Academies Press. The following U.S. EPA graphic shows the relationship between the intrinsic hazard of a pollutant and an assessment of the risk it poses:



http://www.epa.gov/risk_assessment/hazardous-identification.htm.

Chapter VII: Comparison of Pallet Attributes

Based on the results of the Green Screen evaluations, there are a number of flame retardants with safer ratings than decaBDE that could potentially be used in plastic pallets. As the information in previous chapters indicates, however, there are numerous challenges to taking the step from a promising flame retardant to a pallet which both passes fire safety tests and meets the performance needs for a pallet. As specified by DEP, this chapter compares available information on the performance attributes of the following pallets:

- A plastic 48 x 40 shipping pallets containing decaBDE.
- Two plastic 48 x 40 shipping pallets containing non-halogenated flame retardants that have received scores of 2 (use, but search for safer substitutes) in Green Screen assessments.
- Two wood 48 x 40 shipping pallets used for shipping and storing products in the same or similar market sectors (e.g., groceries or other fast turnover consumer goods).

DEP also specified that, if there are no non-halogenated flame retardant 48 x 40 plastic pallets potentially available for use in the same markets currently served by the flame retardant 48 x 40 plastic pallet with decaBDE, then the report should review available information comparing small test specimens of polymers made with decaBDE with similar test specimens made with non-halogenated flame retardants. We have seen that there are now two plastic 48 x 40 shipping pallets using non-halogenated flame retardants – one using a metal hydrate-based flame retardant and the other a proprietary phosphorus-based flame retardant. Therefore this further analysis comparing small test specimens of polymers made with unproven flame retardants is not necessary.

In addition to the pallets above, at least one company (Orbis) is developing a new 48 x 40 pallet with a proprietary, non-halogenated flame retardant, and currently preparing for testing under either UL 2335 or FM 4996. It will be important to track this development over the coming months and, should it be listed under these standards, to screen the flame retardant for potential hazards and review the adequacy of the pallet's performance attributes for use in the open-pool market. Information on this pallet is currently unavailable, so it cannot be included in the comparison for the purposes of this report.

Comparisons of Pallets

Two companies currently manufacture or use plastic pallets with non-halogenated flame retardants that have passed either the UL 2335 or FM 4996 tests to demonstrate fire risk equivalent to or less than that of wood:

- Rehrig Pacific Company, with a UL 2335-certified pallet using a magnesium hydroxide-based flame retardant which includes ATH and zinc borate.
- CHEP (no information on the manufacturer), with a UL 2335-certified and FM 4996-approved pallet using a proprietary phosphorus-based flame retardant that has passed a Green Screen assessment with a '2' .

In addition to comparing, to the extent information is available, the attributes of these two pallets to that of the iGPS/Schoeller Arca Group pallet with decaBDE flame retardant, the comparison will include wood pallets used in open pooling, including both the CHEP wood pallet – which is the most widely used pallet in the open pooling market – and the PECO pallet.

The scope of work for this project requires a comparison of these pallets with respect to the following attributes:[159]

- *Availability in 48-inch x 40-inch dimensions;*
- *Weight;*
- *Load capacity as measured in accordance with the testing methodologies of ISO 8611-1 Pallets for materials handling — Flat pallets and ASTM D 1185 - 98a (reapproved 2009) Standard Test Methods for Pallets and Related Structures Employed in Materials Handling and Shipping;*
- *Expected life in years assuming 5 trips per year and forklift transport;*
- *Susceptibility to breakage and ease of repair;*
- *Weather and moisture resistance;*
- *Recyclability;*
- *Ability to meet the Grocery Industry Pallet Performance Specifications as set forth on page 11 of the Recommendations on the Grocery Industry Pallet System, Cleveland Consulting Associates, 1992;*
- *Ability to accommodate radio frequency identification; and*
- *Cost to users.*

There is some duplication in these attributes, since the GMA specifications[160] cover most of the specifically identified attributes in this list – though not with the specificity of the ISO and ASTM standards. In Table 7.1 below, the attributes of the CHEP flame retardant plastic pallet, the CHEP and PECO wood pallets, and the Rehrig Pacific flame retardant plastic pallet are compared

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[159] Specifications of Work to Be Performed, Task 11.

[160] For the complete text of the GMA Pallet Performance specifications, see Appendix II

with the attributes of the iGPS/Schoeller Arca Group plastic pallet made with a decaBDE flame retardant. Information on the Rehrig Pacific and PECO pallets comes from available product information on their company websites. [161]

The left column lists the attributes from the above list, combining the GMA specifications with the other attributes where appropriate, as almost all of the attributes are found in some form on the GMA list.

Table 7.1: Comparison of Attributes of Plastic Pallets with DecaBDE, Plastic Pallets with Safer Flame Retardants, & Wood Pallets

Pallets/Companies[162]	**iGPS** **HDPE w/ decaBDE** [Information provided by iGPS unless otherwise noted]	**CHEP** **HDPE & PP w/ Proprietary Phosphate** [Information provided by CHEP unless otherwise noted]	**CHEP** **Wood (no flame retardant)** [Information provided by CHEP unless otherwise noted]	**Rehrig Pacific Co.** **PP w/ Magnesium Hydroxide, ATH & zinc borate**[163]	**PECO** **Wood (no flame retardant)**[164]
Pallet attributes[165]					
Availability: 40 " x 48" [GMA #1[166]]	iGPS pallet is 40" x 48"	Yes	Yes	Yes	Yes
4-way entry [GMA #2]	Yes	Yes	Yes	Yes	Yes
12" pallet jack openings & 3&3/4" height clearance under load [GMA #3] [ISO 8611 8.5 Compression deflection test] [ASTM 1185 (98a) 8.5 Deflection Tests]	Yes. 12.5" x 3.5" (40" side) and 14.7 x 3.5" (48" side) with each center block width less than 6"	Yes. Exceeds corresponding ISO 8611 performance standards[167]	Yes. Exceeds corresponding ISO 8611 performance standards	Information not available	Information not available

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[161] The information on the iGPS and CHEP pallets was provided to Pure Strategies by the companies, except where other source noted in footnote. The information on the Rehrig Pacific UL-classified pallet comes from the company's website. For information on the Rehrig Pacific pallet: http://www.rehrigpacific.com/docs/PAL%20008%20060515%2023029%2040x48%20FR%20Rackable.pdf http://www.pdfdownload.org/pdf2html/pdf2html.php?url=http%3A%2F%2Fwww.rehrigpacific.com%2Fdocs%2FBulletin%20PAL%20102%200906%20All%20Pallets.pdf&images=yes . http://pecopallet.com/our_pallets/pallet_specifications.php.

[162] The ISO and ASTM tests listed come from: ISO 8611 (2004 & 2005) "Pallets for Materials Handling – Flat Pallets;" and ASTM D1185 – 98a (Reapproved 2009), "Standard Test Methods for Pallets and Related Structures Employed in Materials Handling and Shipping."

[163] http://www.rehrigpacific.com/docs/PAL%20008%20060515%2023029%2040x48%20FR%20Rackable.pdf

[164] http://pecopallet.com/our_pallets/pallet_specifications.php.

[165] Sources of the attributes (GMA, ASTM and/or ISO) are also indicated in this column.

[166] GMA Grocery Industry Pallet Performance Specifications

[167] With respect to GMA #3, CHEP states that "ISO 8611 performance standards … are more rigorous than GMA."

Pallets/Companies[162]	**iGPS** **HDPE w/ decaBDE** [Information provided by iGPS unless otherwise noted]	**CHEP** **HDPE & PP w/ Proprietary Phosphate** [Information provided by CHEP unless otherwise noted]	**CHEP** **Wood (no flame retardant)** [Information provided by CHEP unless otherwise noted]	**Rehrig Pacific Co.** **PP w/ Magnesium Hydroxide, ATH & zinc borate**[163]	**PECO** **Wood (no flame retardant)**[164]
>85% top surface coverage [GMA #4]	Yes. (97%)	No specific % provided. CHEP says pallet offers better product packaging support than its wood pallets due to honeycomb design	Up to 87% top deck coverage [from website].[168] Utilizes varying top deck designs.[169]	Information not available	Information not available
>60% bottom surface coverage [GMA#5]	No. (57%)	No specific % provided.[170]	55% coverage [from website].[171]	No specific % on website. Reports that pallet has a "large bottom deck surface."	Information not available
Bottom edges chamfered[172] to ¼" [GMA #6]	1/8"	Bottom edges are chamfered	No.[173]	Bottom edges are chamfered	Information not available
Height not >6" [GMA #7]	Yes. (5.62")	Yes.	Yes.	Yes. (6")	Yes. (5.56")
Compatible with pallet conveyors [GMA #9]	Yes	Yes	Yes	Information not available	Information not available
No protruding fasteners [GMA #10]	None used	No	No	None	Information not available
Rack Load capacity, 2800 lbs, and edge rackable in both 40" & 48" dimensions (maximum allowable dimension change (deformation) under weight load) [GMA #15 & 8 ; ASTM 1185 98a 8.4; or ISO 8611-1 8.1.3.1 &2]	Yes. (2,800 lbs)	Yes. (Rated at 2,800 pounds)[174]	Yes. (Rated at 2,800 pounds)	No. (2,000 lbs.)	Yes. (2,800 lbs.)
Stack load capacity, lbs [maximum allowable dimension change (deformation) under 30,000 lbs] [GMA #15, ISO 8611 8.6 or ASTM 1185 8.5]	Yes. (30,000 lbs.)	Yes. (30,000 pounds / dynamic load 5,000 pounds)	Yes. (30,000 pounds / dynamic load 5,000 pounds)	Yes. (30,000 lbs.)	Information not available
Expected life (assuming 5 trips/ year & forklift transport) [GMA #19]	15 years	12 years.[175]	6 years.[176]	Information not available	Information not available

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[168] CHEP specifications for B4840A. http://www.chep.com/getattachment/95c39cdb-2cc1-485c-b1c3-3f747c5e1c08/48x40-Wood-Pallet-%281%29-%281%29.aspx

[169] CHEP responded that "85% top deck coverage is not a current industry standard."

[170] CHEP responded that 60% bottom surface coverage "not a current industry standard." CHEP also noted that both pallets utilize "a perimeter and crucifix design for greater weight distribution than stringer pallets."

[171] Specifications for B4840A

[172] This is an engineering term relating to beveled edges.

[173] CHEP says that chamfered edges for a wood pallet would "lead to excessive pallet damage."

[174] CHEP response for both pallets states that, for rack load, the "company's designed-in safety factor is more than 2x." For edge rackability in both directions, both pallets "include a significant safety factor above rated loads."

[175] CHEP Life Cycle Analysis (peer reviewed) utilized 60 trips.

Pallets/Companies[162]	**iGPS** **HDPE w/ decaBDE** [Information provided by iGPS unless otherwise noted]	**CHEP** **HDPE & PP w/ Proprietary Phosphate** [Information provided by CHEP unless otherwise noted]	**CHEP** **Wood (no flame retardant)** [Information provided by CHEP unless otherwise noted]	**Rehrig Pacific Co.** **PP w/ Magnesium Hydroxide, ATH & zinc borate**[163]	**PECO** **Wood (no flame retardant)**[164]
Susceptibility to breakage Is determined by pallet performance in ISO 8611 9.1:9.2.2, 9.2.3, 9.2.4 or ASTM 1185 98a 9.3,9.4, 9.5	Low damage rate	Meets the ISO 8611 drop tests.[177]	Meets the ISO 8611 drop tests.	Information not available	Information not available
Weather resistant [GMA #17]	UV, moisture, temperature resistant.	FM conducts accelerated weathering tests and pallet passed 4996 standard	FM conducts accelerated weathering tests and CHEP passed 4996 standard	Information not available	Information not available
Moisture resistant [GMA #18]	Made with non-absorbing HDPE (intrinsically hydrophobic)	Yes. Has an open design allowing drainage from blocks.	Standard for industry	Yes	Information not available
Repairs economically feasible [GMA #16]	N/A[178]	Yes	Yes	Information not available	Information not available
Recyclability [GMA #13]	Yes. 100% recyclable	Yes	Yes	Information not available	Information not available
Won't contaminate product [GMA #11]	Non-absorbing (hydrophobic), cleanable/washable, NSF International certified (see notes); not designed for direct food contact.	CHEP observes that the US Food, Drug, and Cosmetic Act does not allow for non-food items (pallets, truck floors, forklifts, etc.) to come into direct contact with food unless they are specifically designed for this purpose. Neither CHEP pallet is designed for such a purpose.		Information not available	ISPM 15 certified
Weight [GMA #14 "Desired weight < 50 lbs."]	Less than 50 lbs. (Approximately 48.5 lbs.)	62 pounds.[179]	Approximately 65 lbs.	49.5 lbs.	Information not available
Approved under FM 4996 or UL 2335 [GMA #12]	FM 4996 Approved and UL 2335 Classified	FM 4996 Approved and UL 2335 Classified	Most all wood. Those with composite block FM 4996 approved	UL-2335 classified	Wood. No listing required.
Accommodates radio frequency identification (RFID)	4 RFID chips in each pallet	Yes; all include RFID	Yes, though most do not contain RFID tags		
Cost to User	Rental Pooled Pallet, Comparable with Wood Pallet Rental Pool	Industry standard range	Industry standard range		

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[176] CHEP Life Cycle Analysis (peer reviewed) utilized 30.3 trips

[177] CHEP's response for both pallets additionally states: "Designed to exceed all industry standard testing, as well as additional, and more rigorous CHEP specific testing."

[178] N/A = not applicable

[179] CHEP response additionally states: "This plastic pallet has a significant amount of steel in the top deck. This additional steel provides significant improvements in deflection."

Using the information from this table, we can summarize the similarities and differences between these pallets, although with information available only from the websites for Rehrig Pacific Company and PECO, there are limits on the comparisons that can be made.

- *Common attributes of all pallets:* There are five areas where all five of the pallets appear to meet industry standards or expectations, even though there may be specific differences: 40" x 48", height, 4-way entry, stack load capacity and fire retardance.
    - With respect to fire retardance, two of the pallets are listed (iGPS, CHEP plastic) as having fire hazards equivalent to or less than wood under both UL 2335 and FM 4996; two others have one of these listings (Rehrig Pacific Company – UL 2335; CHEP wood pallet with composite blocks – FM 4996); while the PECO wood pallet and the CHEP all-wood pallet require no listing.
    - It seems likely that the costs to users of all the open-pooled pallets are in an "industry standard range." As Rehrig Pacific Company sells pallets directly to end users, there is no meaningful way of comparing their prices to the per-use rental rates of PECO, iGPS and CHEP.
    - At least four of the pallets meet the specification of no protruding fasteners; for the fifth (PECO), information on the website didn't address this specification.
- *Rack load capacity:* Four of the five pallets (iGPS, CHEP [both], PECO) meet the rack load capacity of 2,800 pounds, and can be racked in both directions. Rack load capacity of 2,800 pounds is considered an industry requirement for the various products shipped and stored on open pool pallets. So the 2,000 pound rack load capacity of the Rehrig Pacific pallet company, although that can meet needs in a wide range of closed or captive uses,[180] is not sufficient for open pool use.
- *Additional common attributes of the plastic pallets:* All three plastic pallets are moisture and weather resistant. Wood is generally more susceptible to the effects of moisture than plastic. CHEP states that its wood pallet is "standard for the industry."
- *Additional common attributes of the iGPS pallet and both CHEP pallets*: In four additional areas of comparison (susceptibility to breakage, feasibility of cost-effective repairs, recyclability, and height clearance of pallet openings under load), CHEP and iGPS report that their pallets meet relevant GMA, ASTM or ISO standards. While no specific available information addresses these issues for Rehrig Pacific Company or PECO, each may meet some or all of these specifications. For example, refurbishing and repair of wood pallets, with extensive reuse and recycling of pallet components, has dramatically

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[180] GMA's "Recommendations on the Grocery Industry Pallet System" (1992) notes that "approximately 30% of the unit loads weigh less than 1,000 pounds, and 66% of unit loads weigh under 2,000 pounds," GMA, "Recommendations on the Grocery Industry Pallet System," 1992, p. 9.

increased as an industry practice since the late 1990s,[181] and it seems likely that PECO recycles its pallets.

- *Top & bottom surface coverage:* The iGPS pallet meets the GMA specification for top surface coverage, though bottom surface coverage is 3% less than the GMA specification. CHEP states these are not industry standards, and refers to alternative design parameters to achieve the purpose of these standards. Data on the CHEP website states that the wood pallet has "up to 87% top deck and 55% bottom deck coverage."[182] Top deck coverage of 87% would meet the GMA specification; the bottom deck coverage is 5% less coverage than in the GMA specification. Information on the Rehrig Pacific Company website states that the pallet has a large bottom deck surface.
- *Expected Life:* Both CHEP and iGPS estimate substantial durability for their plastic pallets. Using the data provided by the companies, and given the assumption of five trips/year, the estimated life for the iGPS pallet is 15 years, for the CHEP plastic pallet 12 years. For its wood pallet, CHEP estimates 6 years. [No specific estimates were available on the websites for Rehrig Pacific Company or PECO].
- *Weight:* The iGPS and Rehrig Pacific Company pallets both weigh less than 50 pounds, while both wood pallets and the CHEP plastic pallet exceed 50 pounds. (At 62 pounds, the CHEP plastic pallet exceeds the GMA desired weight by 24%).
- *Contamination of product*: The exact wording of the GMA's specification is that the pallet "must be made of material that does not contaminate the product it carries."
    - *DecaBDE flame retardant pallet:* Beyond the general concern for the potential for decaBDE to get into the environment, there is a specific question about contamination of products. To partially address this issue, iGPS contracted with Environ to conduct a study of the transfer of decaBDE from pallets to products while sitting unmoved in storage for 3 weeks. Environ found no observed transfer of decaBDE from polymer pallet surfaces onto product containers.[183] In addition, as noted in Table 7.1, the iGPS pallet has received NSF/ANSI Standard 2 certification under NSF International's Food Equipment Certification Program, which certifies that the design of the pallet will prevent harborage of pests or accumulation of dirt, and permits easy maintenance and cleaning. The standard is for indirect food contact and does not include toxicological testing. With

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[181] Robert J. Bush (Virginia Tech) and Philip A. Araman (USDA Forest Service), "Updated Pallet and Container Industry Production and Recycling Research" SRS 04-CA-11330142-205, October 11, 2008.

[182] http://www.chep.com/getattachment/95c39cdb-2cc1-485c-b1c3-3f747c5e1c08/48x40-Wood-Pallet-%281%29-%281%29.aspx

[183] Environ International Corporation, "Consumer Products Stored on Polymer Pallets Containing Decabromodiphenyloxide: Evaluation of Potential Surface-to-Surface Transfer," prepared for iGPS Company LLC, November 2009.

    respect to direct food contact through a practice such as hydrocooling, iGPS policy is that "we do not authorize use of our pallets for this purpose."[184]
  - *Other pallets:* Wood pallets often raise concerns because of their potential for absorbing spills, harboring insects, etc. These are the types of challenges plastic pallets can help to solve, as evidenced by the NSF certification of the iGPS pallet. For international shipping, wood pallets generally require heat treatment (the alternative of chemical treatment has ended). CHEP notes that the FDA prohibits direct food contact with pallets.
- Accommodation of RFID: Both the iGPS and CHEP plastic pallet are made with RFID chips. The CHEP wood pallet can accommodate RFID, though most do not. RFID can provide real benefits in overall logistics efficiency. At present, system-wide use of RFID is an economic benefit for customers unique to iGPS. CHEP is developing the capacity with some of its pallets, but does not yet have a comprehensive system for all its users.

Of these four alternatives to a decaBDE flame retardant pallet, two (wood or modified wood) are currently in use as open pool pallets, while a third (the new CHEP plastic pallet) will likely be in use for open pool shipping shortly. The Rehrig Pacific Company pallet lacks sufficient rack-load strength to be an open-pool shipping pallet. The iGPS pallet has attributes that none of the alternative pallets match, particularly its light weight. This can reduce shipping costs and reduce ergonomic risks for workers in warehouses, distribution centers or stores in settings where still lighter plastic nestable pallets are not used when pallets require manual handling. In addition, the iGPS RFID system provides a substantial logistics benefit to customers, as well as cost savings in the management of pallets. But on most measures, the CHEP plastic pallet, and in many cases the two wood pallets, matches the attributes of the iGPS pallet.

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[184] iGPS, "iGPS All-Plastic Pallet Receives NSF Food Equipment Certification," July 6, 2010. Personal communication from Mark Sanford, Business Development Manager, Food Equipment Group, NSF International, December 3, 2010. Personal communication from Bruce Torrey, iGPS, via email, December 3, 2010.

Chapter VIII: DecaBDE Plastic Pallets & Functionally Equivalent Alternatives

On the basis of the comparisons in Chapter 7, Maine DEP requires this report to "identify which, if any, of the pallet alternatives are functionally equivalent to plastic pallets containing decaBDE."[185] DEP defines two alternative criteria for a finding that there is an available, "functionally equivalent" pallet.

> *"For the purpose of the study, a pallet will be considered functionally equivalent if:*
>
> - *The pallet meets the Grocery Industry Pallet Performance Specifications as set forth on page 11 of the Recommendations on the Grocery Industry Pallet System, Cleveland Consulting Associates, 1992 or is capable of being manufactured to meet those standards; or*
> - *The pallet currently is used by the grocery industry or other market sectors to ship the same types of good shipped on pallets containing decaBDE."*[186]

This chapter will consider each criterion in turn. As specified by DEP, this review will consider both available plastic and wood pallets.

Criterion #1: Pallet Meets GMA "Grocery Industry Pallet Performance Specifications"

Under this criterion, there is no functionally equivalent alternative pallet to the plastic pallet containing decaBDE.

None of the current potential alternative pallets, neither wood pallets nor the plastic pallet, meets all of the GMA specifications. Using the information related specifically to the GMA specifications from Table 7.1, the following are the specifications that one or more of the pallets do not meet:[187]

- *"Desired weight" limit of less than 50 pounds (GMA #14)*: The wood pallets currently in use in the open pool pallet leasing market both exceed 50 pounds; the CHEP wood pallet is approximately 65 pounds. The new CHEP plastic pallet is 62 pounds. The Rehrig Pacific Company pallet is only 49.5 lbs. The iGPS decaBDE flame retardant pallet, also meets this specification at 48.5 pounds.
- *Top and bottom deck surface coverage of 85% (top surface) and 60% (bottom coverage) (GMA #s 4&5):* CHEP did not provide data for this specification, but stated that neither

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[185] Specifications of Work to Be Performed, Task 12 (as amended 10-13-10)

[186] Criteria in Task 12 of DEP's "Specifications of Work to Be Performed" (as amended 10-13-10)

[187] As noted in the preceding chapter, we have limited data from PECO and Rehrig Pacific Company.

was an industry standard. In the absence of any data provided by the company, we conclude that CHEP wood and plastic pallets may not achieve these specifications (although, as noted in Table 7.1, at least some CHEP wood pallets may achieve 85% top deck surface coverage). The iGPS pallet exceeds the specification for the top surface (97%), and falls 5% short of the specification for the bottom surface (57%).

- *Rack load capacity of 2,800 pounds (GMA #15):* The Rehrig Pacific Company plastic pallet (2,000 pounds) falls short of this goal for rackable strength. Both wood pallets and the CHEP plastic pallet meet or exceed this standard.

- *Must meet or exceed current pallet resistance to fire (GMA #12)*: Since the requirements for resistance to fire are based on equivalence to fire hazards of wood, and FM 4996 and UL 2335 test for equivalence to wood fire hazards, all of these pallets meet this requirement. The CHEP and iGPS plastic pallets have both UL 2335 and FM 4996 listings; the Rehrig Pacific Company pallet has a UL 2335 listing; for those CHEP wood pallets (less than 20%) that have composite blocks with plastic, CHEP has an FM 4996 listing; and the PECO and CHEP all-wood pallets (no composite) require no listing. As discussed earlier in this report, some industry players voiced disagreement with the use of the FM 4996 listing to meet the equivalence requirement. The only NFPA statement on the subject appears to be the unofficial commentary that refers to both standards as allowable at the discretion of local authorities.[188] We were unable to find an authoritative NFPA statement rejecting the applicability of FM 4996 listings.

- *Bottom edges chamfered to ¼" (GMA #6)*: The wood pallets are not chamfered, but the three plastic pallets are.

Table 8.3 summarizes the extent to which various pallets meet the GMA specifications.

Table 8.3: GMA Specification Comparison

Pallet	Weight (lb)	Bottom Surface Coverage	Top Surface Coverage	Rack Load	Fire Resistance	Edge Chamfer
iGPS	**48.5**	**57%**	**97%**	**≥2,800**	UL 2335 & FM 4996	Y
CHEP all wood	**65**	**unknown**	**unknown**	**≥2,800**	N/A	N
CHEP plastic	**62**	**unknown**	**unknown**	**≥2,800**	UL 2335 & FM 4996	Y
CHEP composite block	**65**	**55%**	**unknown**	**≥2,800**	FM 4996	N
PECO all wood	**unknown**	**unknown**	**unknown**	**≥2,800**	N/A	N
Rehrig Pacific plastic	**49.5**	**unknown**	**unknown**	2,000	UL 2335	Y

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[188] NFPA, *Automatic Sprinkler Systems Handbook,* 11th Edition (2010), edited by James D. Lake, p.100.

***Criterion #2: The* pallet currently is used by the grocery industry or other market sectors to ship the same types of good shipped on pallets containing decaBDE.**

Under this criterion, there is a functionally equivalent alternative to plastic pallets containing decaBDE.

Two pallets – the PECO wood pallet and the CHEP wood pallet – are used currently by the grocery industry or other market sectors to ship the same types of goods as are shipped on pallets containing decaBDE. A third pallet, the new CHEP plastic pallet, which just went into production at the beginning of December 2010, has been designed for use in that market. As it is not yet in the market, it is too early to say definitively whether or not it will be used by companies using open pool services to ship the same types of goods, CHEP's market position as the largest open pool pallet company certainly makes this plausible.

Although none of the three pallets meets all of the GMA specifications, as discussed above, a large number of CHEP and PECO wood pallets are nonetheless used to ship the same types of goods as the iGPS pallet. According to the data summarized in Chapter I from Modern Materials Handling magazine (October 2010)[189] the three companies have approximately the following numbers of pallets in open pool use:

- CHEP – approximately 65 million pallets
- iGPS – approximately 10 million pallets
- PECO – approximately 5 million pallets.

While the use of iGPS pallets has grown rapidly, the wood pallets still dominate the open pool market. It is possible that there are particular subsectors currently served by iGPS pallets and not served by the CHEP and PECO wood pallets, but we found insufficient data to make such a determination.

What about the new CHEP pallet? It does not yet have any market share, having only gone into production at the beginning of December. As a plastic pallet with a non-halogenated flame retardant, it provides significant potential for developing another alternative to a decaBDE-based flame retardant pallet in a foreseeable future. CHEP's strength in the open pool shipping market creates a substantial opportunity for accomplishing this. At the same time, CHEP has a substantial commitment to and investment in a market with wood pallets. Much will depend

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[189] Modern Materials Handling Magazine, October 2010 issues: MMH magazine: http://www.mmh.com/article/pallets_and_containers_the_plastic_pool_alternative/, http://www.mmh.com/article/pallets_and_containers_a_chep_off_the_old_block/, http://www.mmh.com/article/pallets_pallet_pooling_for_the_other_guys/.

on the degree to which CHEP aggressively commits itself to production, promotion and use of the new pallet as a strong element of its operations.

What about the fact that all three non-decaBDE pallets exceed, by a substantial amount, the GMA goal that a pallet should be less than 50 pounds? Whatever the undeniable benefits of a lighter pallet, approximately 70 million open-pool wood pallets (about 65 pounds) are currently in use. They provide an alternative to the plastic pallet with decaBDE.

Issues Related to Switching to Alternative Pallets

DEP requires that this report "identify any issues related to switching to … alternatives if the sale of pallets made with decaBDE is banned."[190]

While there are substantial uncertainties about any impacts, since the design and schedule of a ban or phaseout could make a substantial difference, the following seem important possibilities to consider:

- Most important, it would eliminate a significant source of decaBDE that could affect human health and the environment.
- It could create an incentive, and a market opportunity, for pallet manufacturers and pallet management companies to invest in the development of alternative non-halogenated flame retardant pallets that also meet all pallet performance objectives. The combination of state actions and EPA's voluntary agreement with the sources of decaBDE to phase out the flame retardant already seems to be influencing the market. As reported in Table 2.3, at least one other company is currently lining up to test a new pallet with a non-halogenated flame retardant under UL 2335 or FM 4996, although no information is publicly available on the particular flame retardant or the performance characteristics of the pallet.
- Beyond the company currently preparing for the UL and FM tests, the major companies leasing and manufacturing the decaBDE flame retardant plastic pallet, iGPS and Schoeller Arca respectively, are also working on an alternative to that pallet. We have no specific information on the current status of that development, since it is proprietary. Obviously a more competitive market benefits Maine businesses. IGPS and Schoeller Arca bring strong technical expertise and market experience to bear on the options for development and marketing of an alternative pallet, linked with the services iGPS' RFID tracking system provides for their customers. It would be difficult to

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[190] Task 12 of DEP's "Specifications of Work to Be Performed" (as amended 10-13-10). This required task relates to the DEP's obligation under PL 2009, c. 610, §11, to report to the Maine Legislature on issues related to the prohibition on replacing decaBDE with another brominated flame retardant or a chlorinated flame retardant. See 38 MRSA §1606(14)(B)(2).

anticipate how a ban or phaseout of decaBDE in shipping pallets would affect them, especially in the absence of knowing the particular design of such action by the state, and the current status of the effort by iGPS and Schoeller Arca to develop an alternative flame retardant pallet.

- While a large percentage of the market continues to operate with heavier pallets, the weight difference of over 20% between the iGPS pallet and any of the three alternative ones from CHEP or PECO represents, in the absence of a lower-weight replacement, a potential additional shipping expense for businesses and some increased air pollution from trucks.

None of these effects mitigates the need for removing a major source of decaBDE from the environment. But they are issues DEP might consider in determining the timing and design of any ban or phaseout.

Chapter IX: Findings

This chapter presents the findings of this report, and discusses how the structure of this assessment contributed to developing these findings. Finally, this chapter summarizes gaps in publicly available scientific or technical information about potential alternatives to decaBDE.

Report Findings

This section first presents the findings with respect to the central question this report addresses: Are there safer alternative management methods or replacement flame retardants that could eliminate any need for continued use of decabromodiphenyl ether as a flame retardant in plastic pallets? This section will then lay out the specific findings with respect to the tasks in the "Specifications of Work to Be Performed."

Are There Safer Alternatives?

Finding 1: *While there are fire safety systems and management practices for warehouses and other shipping locations that can make the use of flame retardant plastic pallets unnecessary, these are not universally available, and do not provide a comprehensive short-term safer alternative to the use of plastic pallets with flame retardants.*

The NFPA's fire protection standards for warehouses specify sprinkler systems and best management practices for commodities, packaging and pallets that present the most severe fire risks. Warehouses handling these commodities -- including many plastic products, cooking oils, and other highly flammable goods – must establish separate areas of the warehouse that meet the highest levels of protection. These levels would be sufficient for plastic pallets without flame retardants. Some new or modernized warehouses are built entirely with the highest protection levels, and can purchase and use plastic pallets without flame retardants.

But many warehouses, especially older warehouses, meet only minimum NFPA protection requirements. For these warehouses, general use of plastic pallets is only feasible if the pallets are flame retardant. The three open-pool leasing companies (iGPS, CHEP, PECO) moving rapid-turnover consumer products send pallets to warehouses all over the country, a significant proportion of which are not built to the highest possible standards. So the use of open-pool plastic pallets without flame retardants is not currently feasible as a safer alternative to the use of plastic pallets with decaBDE.

Finding 2: '*Safer alternative' non-halogenated flame retardants for plastic pallets are available, and at least one flame retardant plastic pallet meeting essential performance criteria for use in open pool leasing is now in production.*

This study has identified several non-halogenated alternative flame retardants that could potentially be used in plastic pallets and that would be safer for human health and the environment than continued use of decaBDE. One company, CHEP, has just begun production of a plastic pallet with such a safer alternative; the pallet has passed both of the tests (FM 4996 and UL 2335) that list plastic pallets as equivalent to or better than wood for flammability, and meets critical pallet performance specifications. At least one other company is currently scheduling a plastic pallet with an alternative non-halogenated flame retardant for testing under the FM or UL protocol. The emergence of plastic pallets with safer alternatives will allow a reduction in risks to human health and the environment from decaBDE without compromising fire safety.

Additional Findings

Plastic Pallet Manufacturers and Their Use of Flame Retardants (Tasks 1&2; Chapters 1&5)

Finding 3: *Of the twenty-one manufacturers of plastic pallets we identified, most make plastic pallets without flame retardants.*

Only six companies reported manufacturing plastic pallets with flame retardants. In most cases, even for these companies, it is only a small part of their market (e.g., Orbis estimates only 5% of plastic pallet sales with flame retardants).

Finding 4: *The majority of manufacturers of flame retardant plastic pallets use decaBDE as the flame retardant, but that may be changing.*

Four of the six manufacturers of flame retardant plastic pallets currently use decaBDE as the flame retardant. However two of these companies have plastic pallets with non-halogenated flame retardants (proprietary) waiting for tests under the FM 4996 or UL 2335 test protocols. A third company also has a new non-decaBDE flame retardant plastic pallet awaiting testing, but reportedly is substituting another brominated flame retardant for decaBDE.

Finding 5: *The primary polymers for plastic pallets are polypropylene, polyethylene and high density polyethylene.*

These polymers provide a unique blend of processing characteristics and end-use physical properties that enable the production of plastic pallets. These polymers are also commodities and therefore have very favorable economics for a high volume application such as pallets. We identified only one company manufacturing a plastic pallet with a different polymer (PVC), but two companies provided no information on what polymer they are using.

Finding 6: *Much of the information on flame retardant formulas and use is confidential.*

We were unable to obtain information on the amounts of flame retardants used by manufacturers, though the report does include expert estimates of the flame retardant percentages required to make a plastic pallet that could meet both flammability and performance standards.

Industry Use of Plastic and Wood Pallets (Task 10, Chapter 1)

Finding 7: *Direct purchasing and "open pool" leasing of pallets are two largely distinct markets with different demands for pallet performance attributes and flame retardants.*

The largest market for shipping pallets is for sales to companies for their own use, either within their facilities or in a 'closed loop' with other facilities in their own organization or group. The "open pool" leasing market involves shipping of rapid-turnover consumer goods (groceries, beverages, consumer electronics, cleaners, etc.), sent from major producers to different types of warehouses all over the country. Even the approximately 90 million "grocery" (40" x 48") pallets in use in open pool leasing are only a small part of overall pallet use for consumer goods.

Finding 8: *In both open-pool and captive markets, wood pallets represent the overwhelming majority of pallets sold and used.*

Though estimates are very rough, approximately 90% of the entire universe of almost 3 billion pallets is wood. In the open-pool market, there are over 70 million wood pallets managed by two of the three large, open-pool companies (CHEP and PECO), and about 10 million plastic pallets managed by the other large, open-pool company, iGPS.

Plastic Pallets and Warehouse Fire Protection Rules (Tasks 3-5; Chapter 2)

Finding 9: *The National Fire Protection Association (NFPA) establishes standards for preventing and reducing the severity of warehouse fires that form the basis for laws, ordinances* *and regulations for sprinkler systems and best management practices throughout the U.S., including in Maine.*

The NFPA 13 standard, which establishes fire protection requirements for warehouses, provides the basis for state and local warehouse fire prevention laws and is often adopted by reference. In Maine, state warehouse fire protection rules are governed by NFPA. In a few cases (e.g., Scarborough, Gorham, Westbrook), local Maine fire departments regulations have specific provisions that are more stringent than NFPA 13, but none of these relate to plastic pallets.

Finding 10: *Because the polymers (PP, HDPE) used in plastic pallets burn with twice the heat of wood, warehouse fire protection requirements for non-flame retardant plastic pallets are more stringent than those for wood pallets. While warehouses built and managed in accordance with NFPA's highest protection standards can accommodate non-flame retardant plastic pallets (one of the markets for captive direct sale pallets), some of the warehouses receiving open-pool pallets meet minimum, although fully legal, standards that provide too little protection against fire risks from such pallets.*

Because of the added potential intensity of plastics fires, NFPA 13 requires upgraded protection and stricter management for storage facilities using non-flame retardant plastic pallets. For many older or smaller operations, the necessary upgrades would be far too costly. As a result, some warehouses can only accept flame retardant plastic pallets; since open-pool plastic pallets can go to any warehouse, they must be flame retardant.

Finding 11: *The two large scale fire testing protocols, UL 2335 and FM 4996, used to determine whether a flame-retardant plastic pallet can be handled the same way as a wood pallet in a warehouse, are both described in the NFPA 13 Handbook, and by the Maine Fire Marshal Office, as acceptable, but not everyone agrees.*

Both UL 2335 and FM 4996 fire test protocols are used to determine if a plastic pallet is equivalent to wood for purposes of NFPA 13. The tests are different (e.g., both involve tests of idle pallets, but only UL tests pallets loaded with commodities, and only FM 'weathers' specimens to determine if they lose their flame retarding ability). While commentary in the NFPA handbook (which is not an official part of the standard) and most people we contacted accept both, we heard objections that, since FM 4996 doesn't test pallets with commodities, only UL 2335 is acceptable.

Reasons for Selecting DecaBDE or Non-halogenated Alternative Flame Retardants for Plastic Pallets (Tasks 6 & 7; Chapters 3 & 4)

Finding 12: *The three major families of potential flame retardants for plastic pallets are halogenated (predominantly brominated), metal hydrate (e.g., magnesium hydroxide) and phosphorus-based (e.g., ammonium polyphosphate).*

The traditional workhorses have been halogenated flame retardants, though growing regulatory efforts to eliminate the environmental and human health impacts of brominated flame retardants have resulted in increasing research into the other flame retardants.

Finding 13: *When flame retardants are added to plastic, they can have negative effects on key pallet characteristics such as strength, weight and durability, and can make a compound too costly or too unmalleable to process. Industry experts try to design flame retardant/plastic recipes that balance these competing demands. DecaBDE became the flame retardant of choice for many companies because relatively little was needed to be effective; it had fewer adverse impacts on pallet characteristics than other flame retardants; and it was inexpensive.*

When mixed with HDPE, less than 10% decaBDE is required to achieve the required flame retardant protection level for the UL 2335 and FM 4996 tests. Magnesium hydroxide, by contrast, may require as much as 25%, which can severely impact other needed characteristics of the pallet. Until recently, the only non-decaBDE flame retardant plastic pallet on the market was Rehrig Pacific Company's pallet with a magnesium hydroxide-based flame retardant. CHEP has just started to manufacture (December 2010) a proprietary, phosphorus-based flame retardant pallet that has passed UL 2335 and FM 4996. We do not have technical information on either.

Potentially Applicable Flame Retardants for Plastic Pallets (Task 8; Chapter 5)

Finding 14: *On the basis of information provided by flame retardant experts, manufacturers, compounders, and discussions with participants in EPA's Design for the Environment (DfE) workgroup on alternatives to decaBDE for various uses, the most promising non-halogenated flame retardants for toxicological review with the Green Screen, including both primary and supplemental flame retardants, were red phosphorus, ammonium polyphosphate, ethylenediamine phosphate, melamine polyphosphate, magnesium hydroxide, aluminum trihydroxide, zinc borate and magnesium stearate.*

While there is a longer list of potential alternative flame retardants under review by DfE, many are viable alternatives for fabrics or other applications that require very different performance characteristics from those required for plastic in pallets.

Environmental and Human Health Safety of Alternatives (Task 9; Chapter 6)

Finding 15: *The evaluation of the eight non-halogenated flame retardants selected for potential application in plastic pallets demonstrated that several potential alternatives for decaBDE do exist from a human health and environmental safety standpoint.*

Of the eight alternative non-halogenated flame retardants:

- One received a Green Screen score of 4 ("Safer Chemical"): ammonium polyphosphate.
- Six received Green Screen scores of 2 ("Use but Search for Safer Substitutes"): aluminum trihydroxide, ethylenediamine phosphate, magnesium hydroxide, magnesium stearate, melamine polyphosphate, zinc borate
- One received a score of 1 ("Avoid, Chemical of High Concern"): red phosphorus

Assessment of Functional Equivalence of Non-Halogenated Flame Retardant Plastic Pallets and Wood Pallets with DecaBDE Flame Retardant Plastic Pallet (Tasks 11 & 12; Chapters 7 & 8)

Finding 16: *Based on the first DEP criterion for functional equivalence, a strict comparison against all the GMA specifications, there is no functionally equivalent alternative pallet to the plastic pallet containing decaBDE.*

Four pallets meet the criteria established in Task 11 for comparison with the decaBDE flame retardant pallet – two wood pallets used in the open-pool leasing market and two plastic pallets with non-halogenated flame retardants. None of these meet all the GMA specifications. Three (the two wood pallets and the CHEP plastic pallet) exceed 50 pounds, and the fourth (the Rehrig Pacific plastic pallet) does not meet the 2800-pound rack capability requirement. The two CHEP pallets also fall short on top and bottom surface coverage specifications, though the iGPS decaBDE pallet also falls short on bottom surface coverage.

Finding 17: *Based on the second DEP criterion for functional equivalence, that the pallet currently is used by the grocery industry or other market sectors to ship the same types of good shipped on pallets containing decaBDE, there is a functionally equivalent alternative to the plastic pallet containing decaBDE.*

Both the PECO and CHEP wood pallets are currently used in the open-pool market to ship the same types of goods as the decaBDE containing pallets distributed by iGPS. In fact, the CHEP pallet, whether the all-wood pallet or the pallet with composite blocks, dominates that market. In addition, it seems plausible that the CHEP non-halogenated flame retardant pallet that went into production in December 2010 will soon be used in that market.

Structure of Assessment & How Future Assessments Might Be Structured

Maine DEP is participating in a multi-state effort to develop a stronger, more unified approach to the design and implementation of alternatives assessments. Assessments of safer alternatives to the use of toxic chemicals in products often focus primarily on the assessment of available chemical substitutes for the function served by the chemical to be replaced. This is both valuable and extremely important, and in many cases may be the only route to a solution. The use of the Green Screen for this report provided just such an assessment of alternative chemicals that could be used as flame retardants.

But Maine DEP also designed this study to assess the safer alternatives that might be developed through a focus on the structure and operations of the industry. This is not always incorporated as a systematic component of the alternatives assessment. In this study, this meant looking at fire protection systems and pallet management practices that might provide alternatives to the use of flame retardants as a methodology for meeting the requirements of NFPA 13. While, in the short term, the stock of older and less protected warehouses makes a solution based entirely on these factors insufficient, the design helped to broaden the perspective in the study to include ways in which environmental health and fire protection goals could converge in future planning.

Significant Gaps in Scientific or Technical Data on Alternatives

In order to evaluate the alternatives for decaBDE, a direct comparison of the performance characteristics of the pallet as well as the physical properties of the plastic compounds made with non-halogenated flame retardants was needed.

The major challenges to accomplishing this were:

1) *Gathering data on the physical properties of plastic compounds made with non-halogenated flame retardants and decaBDE*. Manufacturers of decaBDE were reluctant to supply data on plastic compounds made with decaBDE. Plastic compounders were reluctant to supply information on proprietary compounds containing flame retardants,

made for pallets. Manufacturers of non-halogenated flame retardants did supply some data that was generated on their products, but comparisons to decaBDE were only available from one manufacturer.

2) *Gathering data on plastic pallets made with non-halogenated flame retardants that are still in the development stages*. This was difficult because pallet manufacturers do not want to prematurely release information on a new product. The pallet performance characteristics are the pallet attributes shown in Table7.1.

- Specific data on physical properties of modulus, impact resistance, melt flow index and specific gravity was generally not available from either manufacturers of plastic pallets or plastic compound manufacturers. The data is necessary to compare the effects of non-halogenated flame retardants and the decaBDE flame retardant on plastic compounds and, consequently, pallets.
- Manufacturers of plastic pallets did not provide specific information on the combinations and concentrations of the flame retardants used in their pallets. However, industry experts provided some general information on the use of decaBDE in plastic pallets.
- Reliable, accurate information on the total market, market segments, the percentage use of plastic pallets, both flame retardant and not, was hard to come by. The most comprehensive study had gaps on the issues related to flame retardance. Available surveys were useful, but targeted at specific audiences rather than the industry as a whole.
- A great deal of information that would be of interest – for example, information on what non-halogenated flame retardants pallet manufacturers are considering and what stage of development they are in – is proprietary.
- Accurate information on the effect of decaBDE on the physical properties of polyolefin plastic compounds from compounders, flame retardant and pallet manufacturers was generally not available. Most data gathered for this report was pieced together from a collection of reports, studies and product information sheets.
- Accurate information from pallet manufacturers on cost issues related to options for development of alternative non-halogenated flame retardants, or on market price constraints on options, is not publicly available. Once again, while such information would be valuable for understanding the incentives that could promote further development of non-halogenated flame retardant pallets, it is proprietary.

Decabromodiphenyl Ether Flame Retardant in Plastic Pallets

A Safer Alternatives Assessment

Appendices

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Appendices: Table of Contents

Appendix 1

Distributors of Plastic Pallets

Company Name	**Address**
Name	Location
Akro-Mils	Akron, Ohio United States
Albion Industries	Albion, Michigan United States
B & R Unifuse	Staatsburg, New York United States
Cadillac Industrial Products Co.	Troy, Michigan United States
Cartonplast LLC	De Forest, Wisconsin United States
Casemaker Inc.	Thornhill, ON Canada
Colson Caster Corp.	Jonesboro, Arkansas United States
Convoy, Inc.	Canton, Ohio United States
Cookson Plastic Molding	Latham, New York United States
Creative Techniques, Inc.	Auburn Hills, Michigan United States
DIC Intl. USA Inc.	Ft. Lee, New Jersey United States
Dynaric, Inc.	Virginia Beach, Virginia United States
EAM Mosca Corp.	West Hazleton, Pennsylvania United States
Faultless Caster	Evansville, Indiana United States
FKI Logistex Automation Div.	Cincinnati, Ohio United States
Flexcon Container	Springfield, New Jersey United States
Frost Inc.	Grand Rapids, Michigan United States
General Container Corp.	Somerset, New Jersey United States

Globe Composite Solutions	Rockland, Massachusetts United States
Goodwrappers	Baltimore, Maryland United States
Gould Plastics, Inc.	Duluth, Georgia United States
Hoover Materials Handling Group, Inc.	Alpharetta, Georgia United States
Intech Corp.	Closter, New Jersey United States
Interroll Corp.	Wilmington, North Carolina United States
IPL Products, Ltd.	Worcester, Massachusetts United States
Jarvis Caster Group	Palmer, Massachusetts United States
JECO Plastic Products, LLC	Plainfield, Indiana United States
Kornylak Corp.	Hamilton, Ohio United States
Linpac Materials Handling	Georgetown, Kentucky United States
LINPAC Materials Handling	Georgetown, Kentucky USA
Lyon Workspace Products	Aurora, Illinois United States
Macro Plastics, Inc.	Fairfield, California United States
Melmat Inc.	Huntington Bch., California United States
Mid-States Engrg. & Mfg., Inc.	Milton, Iowa United States
Molded Fiber Glass Tray Co.	Linesville, Pennsylvania United States
Molded Materials Inc.	Plymouth, Michigan United States
Ohio Rack, Inc.	Alliance, Ohio United States
OptiLogistics, Inc.	Irving, Texas United States
Pacific Bin Corp.	Bellevue, Washington United States
PDQ Plastics, Inc.	Bayonne, New Jersey United States
Plastic Products, Inc.	Schaumburg, Illinois United States
Port Erie Plastics	Harborcreek, Pennsylvania United

	States
Protecta-Pack Systems	Minneapolis, Minnesota United States
Quantum Storage Systems	Opa-Locka, Florida United States
Rampmaster Inc.	Miami, Florida United States
Regplas, Inc.	Mission, Kansas United States
Remcon Plastics, Inc.	Reading, Pennsylvania United States
SCA Packaging North America	New Brighton, Pennsylvania United States
Sealed Air Corp.	Danbury, Connecticut United States
Sealed Air Corp.	Saddle Brook, New Jersey United States
SFB Plastics, Inc.	Wichita, Kansas United States
Shuert Industries Inc.	Sterling Hts., Michigan United States
Signode Packaging Systems	Glenview, Illinois United States
SJF Material Handling Inc.	Winsted, Minnesota United States
SKF USA	Bethlehem, Pennsylvania United States
Smith Companies, Inc.	Pelham, Alabama United States
Sol Plastics. L.P.	Montreal, QC Canada
Superior Tire & Rubber Co.	Warren, Pennsylvania United States
Tente Casters, Inc.	Hebron, Kentucky United States
Timco Inc.	Peekskill, New York United States
Tote Systems Inc.	Burleson, Texas United States
Transpac Corp.	Lansing, Michigan United States
UFP Technologies Inc.	Georgetown, Massachusetts United States
Vestil Mfg. Co.	Angola, Indiana United States

Appendix II

Grocery Industry Pallet Performance Specifications[1]

1) Exact 48-inch x 40-inch dimensions. Square in each direction.

2) True four-way entry. Capable of accommodating existing pallet jacks from all four sides (as opposed to current style with cutouts and stringers).

3) Minimum-width pallet jack openings of 12 inches and minimum height of **3-** 3/4 inch clearance when under load. Width of each center support must be less than six inches to accommodate pallet jacks.

4) Smooth, non-skid, top-bearing surface should have at least 85% coverage. However, 100% is preferred. Non-skid surface should be flat, or have no indentations or protrusions that could cause product damage.

5) Bottom-bearing surface of no less than 60% coverage with properly placed cut-outs (12-inches square) for pallet jack wheels from four sides. Surface should be flat or have no indentations or protrusions that could cause product damage.

6) All bottom entry edges should be chamfered to 114-inch for easy entry and exit.

7) Overall height of platform should not exceed six inches.

8) Rackable from both the 48-inch and 40-inch dimensions. Allowable deflection in drive-in and drive-through racks no more than 112 inch.

9) Compatible with pallet conveyors, pallet dispensers, skate-wheel pallet-flow racks, and automatic storage and retrieval systems.

10) No protruding fasteners.

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[1] Grocery Manufacturers of America, Grocery Industry Pallet SubCommittee (written by Cleveland Associates), ―Recommendations on the Grocery Industry Pallet System," p.11.

11) Must be made of material that does not contaminate the product it carries.

12) Must meet or exceed current pallet resistance to fire.

13) Must be recyclable. Preferably made from recycled material.

14) Desired weight under 50 pounds.

15) Load capacities of 2,800 pounds. Capable of bearing 2,800-pound loads safely in stacks five loads high.

16) Repairs should be economically feasible.

17) Weather resistant.

18) Moisture resistant.

19) Capable of safely moving product, damage free, through the entire distribution channel with multiple cycles (from manufacturer through distributor to retail).

Appendix III

Idle Material Handling Products (FM Approval Class Number 4996)

⊞

The storage of idle material handling products in warehouses or manufacturing facilities can represent a severe challenge to automatic sprinkler protection systems. Products such as pallets, tote boxes, bins or protective cases, especially when manufactured from plastic, wood or cellulosic materials, normally require a very high sprinkler water discharge rate for adequate protection.

While doing extensive research testing, FM Approvals has developed a system and a test methodology to determine if the tested material can be protected as equivalent to wood pallets.

All FM Approved material handling products have been tested according to FM Approvals Standard 4996, "The Classification of Idle Plastic Pallets as Equivalent to Wood Pallets." The Approvals standard specifically addresses idle plastic pallets.

For specific sprinkler protection recommendations, refer to FM Global Property Loss Prevention Data Sheet 8-9, "Storage of Class 1, 2, 3, 4 and Plastic Commodities" and FM Global Property Loss Prevention Data Sheet 8-24, "Idle Pallet Storage."

Approval recognition is extended only to those products which exhibit burning and heat release characteristics equivalent to or less critical than conventional wood pallets. Each FM Approved product shall bear an Approval mark.

...

Plastic Pallets (Class Number 4996)

☑ Group Products by Company

CHEP International Inc
8517 South Park Circle, Orlando, Florida 32819, USA

Product	Listing Country	Certification Type
P4840B	United States of America	FM Approved
B4840A	United States of	FM

Product	Listing Country	Certification Type
	America	Approved

iGPS Company LLC
225 East Robinson St, Suite 200, Orlando, Florida 32801, USA

Product	Listing Country	Certification Type
BiPP4840 HR 6R iGPS Pool Pallet	United States of America	FM Approved

Orbis Corporation
1055 Corporate Center Dr, Oconomowoc, Wisconsin 53066-0389, USA

Product	Listing Country	Certification Type
Model 1200x1000 (39x47) FM SuperPal	United States of America	FM Approved
Model 36 × 42 FM FG	United States of America	FM Approved
Model 36 × 48 FM FG	United States of America	FM Approved
Model 40 × 48 FM BulkPal	United States of America	FM Approved
Model 40 × 48 FM HDSC	United States of America	FM Approved
Model 40 × 48 FM RACK’R	United States of America	FM Approved
Model 40 × 48 FM RCKO	United States of	FM

Product	Listing Country	Certification Type
	America	Approved
Model 40 × 48 FM RCKO LP	United States of America	FM Approved
Model 40 × 48 OP FM CIISF	United States of America	FM Approved
Model 40 × 48 OP FM CIISF LP	United States of America	FM Approved
Model 40x48 Stack'R Pallet	United States of America	FM Approved
Model 42 × 48 FM HDSC	United States of America	FM Approved
Model 44 x 56 DC HI	United States of America	FM Approved
Model 44 x 56 DC LO	United States of America	FM Approved
Model 44 x 56 OCP	United States of America	FM Approved
Model 45 × 48 FM HD Lip A	United States of America	FM Approved
Model 45 × 48 FM HD Lip B	United States of America	FM Approved
Model 45 × 48 FM HD Lip C	United States of America	FM Approved
Model 45 × 48 FM JOURNEY	United States of America	FM Approved
Model 48 × 48 FM Drum OP CIISF	United States of America	FM Approved

Product	Listing Country	Certification Type
Model 48 × 48 FM HD DRM	United States of America	FM Approved
Model 48 × 48 FM HDSC	United States of America	FM Approved
Models 40 × 48 FM GrabPal 2.5”,3.7,” GrabPal 3.0” con	United States of America	FM Approved

Plastics Research Corporation
1400 South Campus Ave, Ontario, California 91761-4330, USA

P/N 105250-101 is a high performance composite pallet designed to comply with GMA requirements for a 40 x 48 in (1 x 1.2 m), 4-way, rackable, non-reinforced pallet, capable of multi-trip duty. This pallet does not contain decca-bromine.

Product	Listing Country	Certification Type
P/N 105250-101 Plastic Pallet	United States of America	FM Approved

Polymer Solutions International
15 Newtown Wood Road, Newtown Square, Pennsylvania 08055, USA

Product	Listing Country	Certification Type
4048 Prostack general purpose plastic pallets	United States of America	FM Approved
4048 Prostack with Lip general purpose plastic pallets	United States of America	FM Approved
4048 Prostack with Cleat and Corner Openings plastic pallets	United States of America	FM Approved

Schoeller Arca Systems Inc
3000 Town Center, Suite 620, Southfield, Michigan 48075, USA

Product	Listing Country	Certification Type
BiPP4840 HR 6R iGPS	United States of America	FM Approved

TMF Corporation
850 West Chester Pike, Suite #303, Havertown, Pennsylvania 19083-4439, USA

Product	Listing Country	Certification Type
Model Protech 4048	United States of America	FM Approved

Appendix IV: UL 2335 Classified Pallets

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Guide Information	Pallets, Storage	*QENL.GuideInfo*
POLYMER PALLETS L L C	Pallets, Storage	*QENL.R19299*
REHRIG PACIFIC CO	Pallets, Storage	*QENL.R20575*
SCHOELLER ARCA SYSTEMS INC	Pallets, Storage	*QENL.R25482*

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QENL.R25484

Pallets, Storage

See General Information for Pallets, Storage

CHEP EQUIPMENT POOLING SYSTEMS R25484

8517 S PARK CIR

ORLANDO, FL 32819 USA

Pallet Name	General Description	Pallet Length (inches)	Pallet Width (inches)
P4840B - V2.0	Four-Way Entry, Block Pallet	48	40

Last Updated on 2010-12-17

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Pallets, Storage

See General Information for Pallets, Storage

POLYMER PALLETS L L C R19299

U S 422

15567 MAIN MARKET RD

PO BOX 674

PARKMAN, OH 44080 USA

Pallet Name	General Description	Pallet Length (inches)	Pallet Width (inches)
Polymer Pallet	PVC Two-Way Entry, Stringer Pallet	48	48
Polymer Pallet	PVC Two-Way Entry, Stringer Pallet	48	42
Polymer Pallet	PVC Two-Way Entry, Stringer Pallet	42	48

Polymer Pallet	PVC Two-Way Entry, Stringer Pallet	44	44
Polymer Pallet	PVC Two-Way Entry, Stringer Pallet	48	40
Polymer Pallet	PVC Two-Way Entry, Stringer Pallet	40	48
Polymer Pallet	PVC Two-Way Entry, Stringer Pallet	42	42
Polymer Pallet	PVC Two-Way Entry, Stringer Pallet	36	48
Polymer Pallet	PVC Two-Way Entry, Stringer Pallet	40	40
Polymer Pallet	PVC Two-Way Entry, Stringer Pallet	36	36
Polymer Pallet	PVC Four-Way Entry, Block Pallet	48	48
Polymer Pallet	PVC Four-Way Entry, Block Pallet	48	42
Polymer Pallet	PVC Four-Way Entry, Block Pallet	42	48
Polymer Pallet	PVC Four-Way Entry, Block Pallet	44	44
Polymer Pallet	PVC Four-Way Entry, Block Pallet	48	40
Polymer Pallet	PVC Four-Way Entry, Block Pallet	40	48
Polymer Pallet	PVC Four-Way Entry, Block Pallet	42	42
Polymer Pallet	PVC Four-Way Entry, Block Pallet	36	48
Polymer Pallet	PVC Four-Way Entry, Block Pallet	40	40
Polymer Pallet	PVC Four-Way Entry, Block Pallet	36	36

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See General Information for Pallets, Storage

REHRIG PACIFIC CO R20575

4010 E 26TH ST

LOS ANGELES, CA 90023 USA

Pallet Name	General Description	Pallet Length (inches)	Pallet Width (inches)
HuskyLite Snap-Lock Pallet	Four-Way Entry, Block Pallet	48	40
HuskyLite Snap-Lock Pallet	Four-Way Entry, Block Pallet	48	36
HuskyLite Snap-Lock Pallet	Four-Way Entry, Block Pallet	43	37
HuskyLite Snap-Lock	Four-Way Entry, Block	41.3	37.4

Pallet	Pallet		
HuskyLite Snap-Lock Pallet	Four-Way Entry, Block Pallet	37	37

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QENL.R25482

Pallets, Storage

Pallets, Storage

See General Information for Pallets, Storage

SCHOELLER ARCA SYSTEMS INC R25482

SUITE 110

5202 OLD ORCHARD RD

SKOKIE, IL 60077 USA

Pallet Name	General Description	Pallet Length (inches)	Pallet Width (inches)
BiPP 4840 HR 6R iGPS PoolPallet-SAS	Four-Way Entry, Block Pallet	48	40

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Appendix V

Polymer Range for Flame Retardant Plastic Pallets

Prepared for this report by:
James Innes & Ann Innes
Flame Retardants Associates

The polymer resins most likely to be chosen by a formulator for the flame retardant plastic pallet application include the polyolefins (PP, PE) and/or MPPO. The polyolefin resins are from a technical perspective the easiest to flame retard while retaining the physical properties required for a plastic pallet AND doing so at the least cost to produce.

Further, after significant review of flame retardant plastic pallet technology and marketplace, it is apparent to the authors that only two specific polyolefin polymer resins will practically fit the flame retardant plastic pallet application. These are HDPE, high density polyethylene, and polypropylene copolymer or impact modified polypropylene. The process for making the pallet is injection molding (although there are some thermoformers). The pallet making process largely governs the selection of melt flow of the chosen polymer. The polymer must be able to be injection molded in such a process; i.e., melt flow appropriate for the process. Either virgin resin or post-industrial recycle resin would be chosen. Of importance to note is that HDPE is the resin found in most post-consumer PE as it is used in the overly- abundant milk containers sold across the country. This is a blow molding grade and is <u>not</u> applicable to injection molding. The table below is an abbreviated list of polypropylene and HDPE suppliers, trade names and grades of HDPE that could fit the flame retardant plastic pallet application.

HDPE Suppliers, Trade Names, HDPE Grades

Suppliers	**Trade Names**	**Grades/Comments**
Chevron Phillips	Marlex HWN4550 HDPE 5 MFI*	Tensile Strength 3500^+ psi Flex Modulus 160-180 (10^3 psi ASTM D790) Izod Impact 6^+ fl lb/in (Notched)
Equistar Chemicals LP	Alathion M4661 HDPE 6 MFI	
Exxon Mobil	Escorene HD 6705 HDPE Escorene HD 0358 HDP	
Ineos	Fortilene KG4685 PP	
Phillips Sumika	Marlex AGN120	
Equistar Chemicals	Petrothene PP38NR01X01	
Lyondell Basell	Moplen EP340M	

*MFI = Melt Flow Index

In the 1990's GE Plastics, now SABIC, developed several new applications for their Noryl® polymer. This included a "plastic house" and they did also develop a plastic pallet which actually went through the requisite pallet testing at FM to prove the formulation met the FM standard for idle pallets. Noryl® is modified polyphenylene oxide (or ether) blended with high impact polystyrene or HIPS. The amount of HIPS in the formulation depends on the flow needed for the application. In addition to these two polymers, the formulations also include 10-15% of a phosphate ester plasticizer which results in a UL94 V0 formulation. [A lower loading (~6-8%) of the phosphate ester would likely result in a pass in the idle pallet test; however, physical properties would require consideration.] Various plasticizers have been used since the initial development. Most recently, these have been alkylated phenol phosphate or bisphenol A diphosphate. The pallet produced was deemed to be too expensive to market and, as a result, GE did not renew the certification with FM and did no further development. Flame Retardants Associates estimates that a pallet produced with Noryl® which meets the pallet standards would be in the economically prohibitive range of over $90/pallet. Also, there is little or no post-industrial MPPO available in the recycle marketplace which could result in lower cost.

Appendix VI

The Cost Factor and Flame Retardant Plastic Pallets

Prepared for this report by:
James Innes & Ann Innes
Flame Retardants Associates

Specific gravity is an important concept to understand. Why? Because it directly impacts the cost factor for producing a pallet. Indeed, it is the controlling part of the cost factor. Specific gravity can be defined as the density (mass per unit volume) of any material divided by that of water at a standard temperature (usually 4°C). Since water's density is nearly 1.00 g/cc, density in g/cc and specific gravity are nearly equal.

What does this mean? For a given volume of material, a plastic compound with a lower specific gravity will produce a part with lower weight. Or it actually takes less pounds of material to fill a mold to produce the part. A given amount of a plastic compound or formulation with a lower specific gravity will produce more parts than another formulation with a relatively higher specific gravity. Molds are filled on a volume basis, not weight. One of the resulting "tricks of the trade" is knowing that a less costly formulation which meets all the part's requirements across the board may simply not be economically attractive if its specific gravity is too high. In other words, needing more of the compound to fill the mold often wipes out the advantage of the lesser cost per pound.

From this point forward, a review of formulation costs incorporating the absolutely required specific gravity factor will be presented. This should help the reader understand how to do the cost calculation as well as the direct impact on cost of specific gravity.

If a 40" x 48" rackable standard pallet weighs 44.2 pounds using a non-flame retardant PP resin, flame retardant (FR) versions will produce pallets weighing amounts different than that. See Table App-VI-1 for the calculations which incorporate specific gravity data. These calculations assume a 0.9 specific gravity for the PP resin and a 0.95 specific gravity for the DECA/antimony trioxide FR system, and 1.048 for the MDH FR system.

Table App-VI-1. Calculating the Weight of FR Plastic Pallets

PP Pallet (no FR) Weight	Weight of Pallet with Deca/Antimony as FR	Weight of Pallet with MDH as FR
44.2 pounds	44.2/0.9 x 0.95[1] = 46.65 pounds	44.2/0.9 x 1.048 = 51.46 pounds

[1] Let's assume a 50 pound pallet which contains 3.4 pounds of DECA and 1.133 pounds of antimony trioxide (this is a 3 to 1 ratio). A formulator would probably do a calculation using an even 100 pounds. So the calculation of the 0.95 specific gravity for the DECA/antimony/PP system is obtained as follows:

90.934 pounds PP sp grav of 0.9	0.90934/0.9 = 1.0103 cc (cubic centimeters)
6.8 pounds DECA sp grav 3.25	0.068/3.25 = 0.0292 cc
2.266 pounds antimony trioxide sp grav 5.6	0.02266/5.6 = <u>0.0040 cc</u>
	Total cc = 1.0435 cc

Or for the DECA FR system 1/1.0435 = 0.095 sp gravity

The iGPS Pallet

Now, as an example, let's look at some hypothetical calculations for the iGPS FR pallet, starting with specific gravity.. This pallet is made from HDPE, not PP, and is flame retarded with a DECA/antimony trioxide system. It contains about 3.4 pounds DECA and is expected to contain 1.133 pounds antimony trioxide using a 3 to 1 ratio (which is typical for this system). Let's convert this 48.5 pound pallet to a formulation batch weighing 100 pounds to make the calculations easier.

3.4 pounds DECA/ 48.5 pounds pallet mass = 7.01% loading (let's round that to 7.0)

1.133 pounds antimony trioxide/48.5 pounds pallet mass = 2.37% loading

We have 7 pounds of DECA + 2.37 pounds of antimony trioxide = 9.37 pounds. So in a 100 lbs batch, that means we have 90.63 pounds of HDPE (or this is a 90.63% loading).

We know the specific gravity of HDPE ranges from 0.952 to 0.965, so let's use 0.96 for our calculation here.

0.9063 HDPE/0.96 sp grav = 0.9440

0.070 DECA/3.25 sp grav = 0.0215

0.0237 Sb_2O_3/5.6 sp grav = <u>0.0042</u>

Total = 0.9697 cc/gram

1/0.9697 = **1.0312** specific gravity for this DECA/Antimony HDPE formulation. This is the density of this formulation in grams per cc.

Now let’s move on to some cost calculations for this iGPS DECA FR HDPE pallet.

A simple calculation of total formulation raw material cost per pound using the raw material component costs would be done as shown in Table 14. In this table, the colorants/stabilizer cost/pound was gathered from current commercial stabilizer/colorant suppliers.

Table App-VI-2. Simple DECA FR HDPE formulation cost calculation

Formulation Component	Loading	Cost/pound	Component Cost
HDPE	88.63%	$0.80	$0.709
DECA	7.0%	$1.80	$0.126
Antimony Trioxide (Sb_2O_3)	2.37%	$3.00	$0.0711
Colorants/Stabilizers	2%	$2.50	$0.05
Formulation Total Cost/pound			$0.9561

But the reality of actually trying to produce a formulation like this and push it into an injection molding machine to produce a large part like a pallet means that in all likelihood a masterbatch would be used. This masterbatch (think concentrate) is let down in the pallet injection molding machine at a loading level that produces the required amount of FR system in the formulation being injected into the pallet mold. A masterbatch is produced by a masterbatch compounder. See Figure App-VI-1 for a list of known commercial suppliers of masterbatch compound. Each has supplied a full range of masterbatch needed for plastic pallet manufacture.

Masterbatch Supplier	**Location**
Spartech Polycom	Denora, PA
Washington Penn Plastics	Washington, PA
PolyOne Corporation	Avon Lake, OH
Phoenix Plastics	Conroe, TX
Saco Polymers (formerly Padanaplast)	Aurora, OH
Hanson Company	Duluth, GA

Figure App-VI-1. Commercial Masterbatch Suppliers

A typical masterbatch would contain 60% active FR in a HDPE. See Table App-VI-3 for the masterbatch cost calculation.

Table App-VI-3. DECA/Antimony Trioxide HDPE Masterbatch Cost Calculation

Formulation Component	**Loading**	**Cost/pound**	**Component Cost**
HDPE	40%	$0.80	$0.32
DECA	44.82%	$1.80	$0.806
Antimony Trioxide (Sb_2O_3)	15.18%	$3.00	$0.455
Formulation Total Cost/pound			$1.581

The cost calculation for this masterbatch plus the cost to compound plus a markup for profit gives a good estimate of the sell price per pound of this masterbatch to the pallet molder. In this case, let's assume $0.20/pound as a cost of compounding which gives a cost of $1.781/pound for the masterbatch producer to produce this formulation. The masterbatch producer will mark this up to make a profit so let's assume a 30% markup. This produces a cost per pound to the pallet injection molder of $2.54. Now let's use this cost and recalculate in Table App-VI-4 the raw material cost for the iGPS FR pallet (in other words, we are now re-doing the calculation costs in Table App-VI-2 to reflect real world use of masterbatch). To provide the required 7% DECA in 100 pounds of the final compound, 15.61 pounds of the $2.54/pound masterbatch will be required. (7% / 44.82% = 15.6%)

Table App-VI-4. Pallet Formulation Cost Calculation Using Deca FR Masterbatch

Formulation Component	**Loading**	**Cost/pound**	**Component Cost**
HDPE	82.39%	$0.80	$0.659
DECA Masterbatch	15.6%	$2.54	$0.396
Colorants/Stabilizers	2%	$2.50	$0.05
Formulation Total Cost/pound			$1.105

So a better estimate of the raw material cost per pound for the Deca FR pallet is $1.105 rather than the $0.9561 computed in Table App-VI-2.

More Costs – Plastic Resins and Plastic Pallets

The cost of producing a flame retardant plastic pallet varies significantly depending on the base resin and the chosen flame retardant. Table App-VI-5 shows price ranges for three of the more likely resins for the FR plastic pallet application. [Plastics News, 9/27/10, pp. 21-22]

Table App-VI-5. Price Ranges for Likely Plastic Pallet Resins

Resin	Grade/Description	Price range/pound
HDPE	Injection Molding Recycle	\$0.80-\$0.85 \$0.41-\$0.45
PP	Injection General Purpose Large Buyers* Recycle Industrial	\$0.97-\$1.03 \$0.66 - \$0.67 \$0.62-\$0.68
PPO/PPE	Injection General Purpose	\$1.23-\$1.87

*London Metals Exchange for very large buyers, Plastics News, Sept 6, 2010

Cost to purchase pallets in the pallet industry today ranges from \$5 per pallet for a wood pallet to \$60 per pallet for a 50 pound plastic (non-FR) pallet to a halogen FR pallet at about \$100 per pallet which weigh about 55 pounds.

Plastic Pallet using a Metal Hydrate FR system

Now let's look at the cost to produce a plastic pallet using PP and a MDH (magnesium hydroxide) non-halogen flame retardant. Since we now live in the real world, we need to calculate a masterbatch cost first. See Table App-VI-6.

Table App-VI-6. Cost Calculation for non-halogen FR Masterbatch

Formulation Component	Loading	Cost/pound	Component Cost
PP	28%	\$1.00	\$0.28
MDH	70%	\$0.35	\$0.245
Processing Aid	2%	\$1.20	\$0.024
Formulation Total Cost/pound			\$0.549

Adding a $0.20 cost to compound gives a cost to manufacture of $0.749 per pound. Add a 30% markup for a price to the pallet molder of $1.07 per pound.

To provide 23% MDH in the final compound, 40 pounds of masterbatch will be used. So now we can compute the cost of raw materials. See Table App-VI-7.

Table App-VI-7. Raw Material Cost for a MDH FR PP Pallet using a PP FR Masterbatch

Formulation Component	Loading	Cost/pound	Component Cost
PP	58%	$1.00	$0.58
MDH-PP Masterbatch	40%	$1.07	$0.428
Black Masterbatch	1%	$2.00	$0.02
UV Thermal Concentrate	1%	$3.00	$0.03
Formulation Total Raw Material Cost/pound			$1.058

Let's look at specific gravity calculations for this non-halogen FR PP approach.

For the masterbatch, we have (let's leave out the process aid for this calculation):

PP at 0.28/0.9 sp grav = 0.3111 cc and MDH at 0.70/2.36 sp grav = 0.2966 cc for a total of 0.6077 cc/gram or 1.6455 grams per cc.

For the final MDH FR PP, we have:

PP at 0.58/0.9 sp grav = 0.6444
MDH Masterbatch at 0.4/1.6455 = 0.2431
Additives at 0.02/0.9 = <u>0.0222</u>
Total = 0.9097 or 1/0.9097 = 1.0993 grams/cc (sp gravity)

So for a comparison, the density of the DECA containing iGPS HDPE pallet was 1.0312 while the density for our MDH FR PP pallet is 1.0993. So if iGPS or anyone else were to make a FR plastic pallet from our MDH FR PP formulation, the weight of that pallet in the same mold used for the iGPS pallet would be calculated as follows:

48.5 pounds x 1.0993/1.0312 = 51.7 pounds

Therefore, the non-halogen FR PP pallet made in the iGPS mold goes a little over the 50 pound mark (which is the recommended upper weight limit by the GMA).

What about using a phosphorus FR system in a plastic pallet?

The use of phosphorus flame retardants such as APP, APP derived compounds, and EDAP have not really found application in non-halogen FR plastic pallets, or many other applications for that matter. This is likely mostly due to first the fact that halogen FR's continue to be used and are cost/performance effective and secondly to a perception that phosphorus FR systems are just too costly. However, they may very well be worth taking a look at in a plastic pallet application since the flammability requirement, "burn like wood", is far lower than a more stringent requirement to be self-extinguishing. So let's take a look at the cost situation for EDAP as an example.

The cost for a typical FR PP formulation using EDAP , such as Unitex FR44-94S, that is expected to meet idle pallet requirements (this formulation has not been tested in this type of test as far as the authors know) would be calculated as in Table App-VI-8.

Table App-VI-8. Cost Calculation for an FR PP Formulation using EDAP

Formulation Component	**Loading**	**Cost/pound**	**Component Cost**
PP	86%	$1.00	$0.86
EDAP	12%	$2.50	$0.30
Stabilizers	2%	$2.50	$0.05
Formulation Total Raw Material Cost/pound			$1.21

With the $0.20/pound compounding cost and 30% profit, we have a cost to the pallet producer of $2.01/pound.

Specific gravity of EDAP is 1.3. The formulation specific gravity is:
PP at 0.86/0.9 sp grav = 0.9555
EDAP at 0.12/1.3 = 0.0923
Additives at 0.02/0.9 = 0.0222
Total = 1.07 or 1/1.07 = 0.9346 grams/cc (sp gravity)

A disadvantage of this system is that the EDAP compound cannot be introduced using a masterbatch but must instead be added during the compounding operation. (A second heat history is not a good thing when it comes to phosphorus compounds.) Recall that for the DECA and metal hydrate FR systems, a masterbatch can be used.

The same formulation might also work with HDPE as the resin. In such a case, the specific gravity of the formulation would be:

HDPE at 0.86/0.96 sp grav = 0.8958
EDAP at 0.12/1.3 = 0.0923
Additives at 0.02/0.9 = 0.0222
Total = 1.0103 or 1/1.0103 = 0.99 grams/cc (sp gravity)

So what does all of this mean? It means that since the iGPS pallet weighs about 48.5 pounds and has a specific gravity of 1.0312 (see highlighted result on p. 24 above), then this HDPE-EDAP formulation with a specific gravity of 0.99 would produce a pallet that weighs 46.6 pounds. (48.5/1.0312 x 0.99)

The net result then is the iGPS pallet made using the DECA masterbatch would cost 48.5 pounds of material times the HDPE-DECA cost of $1.105/pound or $53.59. Whereas the HDPE-EDAP formula pallet weighs 46.6 pounds with a cost of material to the pallet producer of $2.01/pound or a price of $93.66. So herein lays the drawback to the phosphorus approach. The final cost is prohibitively high – at least in comparison to other options. The same problem occurs when considering APP with a specific gravity of 1.8 and a HDPE-APP formulation cost equivalent to the HDPE-EDAP cost of $2.01/pound. The pallet weight is slightly higher at about 47.8 pounds and the cost is still above $90 per pallet.

So in summary it seems logical to conclude that a non-halogen FR plastic pallet is going to have to start with a metal hydrate, probably magnesium hydroxide, and a polyolefin resin, probably PP. ATH could be used as well but temperatures must be kept low and so the resin with this FR must be HDPE (as PP is processed above the ATH water release temperature). Polypropylene is a little more costly on $/pound purchase price than HDPE, but hopefully we have now learned that the initial cost per pound has nothing to do with the cost of the material going into the mold. The cost and specific gravity calculations must be performed first to get a true picture of the cost to fill the pallet mold.

The exact formulation components and cost numbers in the real world will be different than those shown here because we have simplified the formulations to make it easier to understand the calculation principles and because prices fluctuate on a daily basis for almost all materials. The important thing to learn is that there is a lot involved in developing a balanced formulation. When flame retardants are loaded into formulations, especially those needing to meet more stringent flammability standards (more stringent than "burn like wood"), the physical property most impacted is tensile strength. The tensile strength goes down and translated to a pallet in use, this means it will be more likely to break under load. However, at the reduced FR loadings needed for a FR plastic pallet, the adverse impact on tensile strength as well as other properties is lessened considerably. (This helps support the argument that making a non-halogen FR plastic pallet is feasible.)

Appendix VII: Innovative and Novel Non-Halogen Flame Retardants

Nicholas A. Zaksek, Manager of Applications Research and Development, JJI Technologies

[Paper presented at ANTEC 2010 by David Diefenthal and sponsored by Society of Plastic Engineers]

Abstract

JJI Technologies bases its technology platform on developing innovative and novel non-halogen flame retardants and plastic additives. Our self-catalyzed technology embedded within the flame retardant enhances physical performance, increases extinguishing efficiency, and simplifies the compounding process. Our JJAZZ™FR boasts features such as low smoke and odor when exposed to flame. This is achieved by forming a robust char barrier that stops the flame from propagating to the polyolefin. Features such as a low specific gravity, lower loading levels, and non-blooming help to exemplify the overall cost savings and improved aesthetics that benefit the user.

Introduction

The demands for flame retarded materials continues to increase with building material and electrical component markets pushing toward the use of polymers in increasing numbers of end applications. There are 3 basic constituents that must be considered when flame retarding polymers; the effectiveness of the flame retardant, the physical properties, and the sustainability of the product throughout its life cycle.

In most applications, the additions of non-halogen flame retardants are considered to be fillers as opposed to an additive. This is especially true in the case of metal hydroxides and hydrates where the loadings comprise of more than fifty percent of the polymer system. The addition of filler to a polymer often dramatically impacts the physical properties of the polymer. The effectiveness of the flame retardants to reduce flame spread, smoke generation, and in many cases extinguish the flame establishes its value in the market. The necessary loading of the flame retardant to meet the demands of stringent flame tests, also effects the latter. Finally, sustainability has become a rapidly increasing concern among plastic compound manufacturers as well as flame retardant producers. Regulations are driving initiatives to recycle and preserve the environment. The importance of “green” products has become more prevalent than ever before.

Flame retardants can no longer maintain a pristine image by proving safe in their usable form. They are scrutinized from the point of manufacturer, how safe they are for exposure to humans and pets, what by-products occur when they burn (i.e. toxic smoke, carcinogens), and their end of life. Bioaccumulation, decomposition products, heavy metals, small molecules, halogens, PBB and PBDE’s, and recyclability are all concerns that the new generations of flame retardants have to answer too.[1] This paper serves to illustrate that through innovative knowledge and technology; JJI Technologies is developing and improving its flame retardant additives to meet the demands of the market and its customers.

JJAZZ Physical Properties

JJAZZ™ is a free flowing white powder available in three particle sizes to meet physical and dielectric application demands (Figure 1, 2). The powder is a neutral pH and exhibits a low specific gravity to reduce compound weight. With the lower loading levels needed to flame retard a compound, it is easy to color. The aesthetics of products are also enhanced since the JJAZZ™ does not exhibit any surface migration. All of the properties contribute to an efficient flame retardant that is non-toxic, generates less smoke, and is fully recyclable. A chart illustrates a full comparison of JJAZZ™ as well as other products JJI currently has in development (Figure 3).

Results and Discussion

Upon investigating traditional non-halogen flame retardants, metal hydroxide and hydrate flame retardants are limited due to the excessively high loading necessary to achieve acceptable performance results. These excessively high loadings significantly impact physical properties as well as adding weight to the final compound.[2] Intumescent flame retardants, like those in the ammonium polyphosphate family, allow loading levels to be reduced, thus preserving the properties of the base resin. Unfortunately, most of these flame retardants need a synergist, usually a pentaerythritol, which needs to be added congruently for the system to be fast-acting and completely effective. This synergist has proven to be the Achilles heel of these FR’s due to it being hydrolytically weak coupled with the inability to insure full dispersion (Figure 4).[3]

Mechanisms

The reason for the addition of a synergist lies in the mechanism of how intumescent systems work. They are comprised of three components: an acid source (APP), a carbon source (pentaerythritol), and a blowing agent (typically melamine) which all need to interact with each other in a prescribed sequence of events[4, 5]. The acid source breaks down to dehydrate the carbon source. Once this process is complete; the blowing agent has to decompose in order to form a protective heat sink char[6].

JJAZZ™ not only utilizes the above method of action, but also reacts to form nitrogen gas to dilute the fuel source and prevent the acid source from volatizing away before it can react with the carbon source.

Char Formation

JJAZZ™ has overcome the hurdles noted above by embedding a proprietary catalyst to eliminate the need for the addition of a synergist. This self catalyzing technology ensures good distribution at a molecular level (Figure 5). This allows for superior distribution and functionality within the polymer which decreases loading levels. Also this would improve the physical properties of the final product. The technology also serves two additional purposes; it creates low activation energy and a fast deploying char. JJAZZ™ also creates a dual layer char consisting of initially a hard and glassy char, accompanied by a porous and highly insulating char upon continued exposure to flame. This unique mechanism may require additional additives in a standard FR system. This is clearly illustrated by the two maximum decomposition point shown by TGA analysis (Figure 6).

JJAZZ™ Performance Data

All performance data will vary due to resin selection, the final application, and the additives package that is utilized in the compound. Several addition levels of JJAZZ™ were compounded on a 50mm twin screw extruder in a 7 melt flow rate polypropylene to illustrate the minimal impact JJAZZ addition has on the final compound. These loading levels are in accordance with tests that require more stringent and rigorous burn testing requirements. One additional note is that the melt flow rate was measured at a lower temperature in order to keep the FR from prematurely activating. The data is listed in a chart below (Figure 7).

Processing Parameters

JJAZZ™, like other phosphorous based FR's, does have processing limitations and is therefore limited to polyolefins and some rubber compounds. Typical processing temperatures on an extrusion unit should not exceed 390°F (~200°C). JJI Technologies provides support on proper extrusion parameters in order to achieve the optimal compound results (Figure 8, 9).

Continued R&D

It has been noted that not one flame retardant can fill every need. The key to success of the application is optimizing intumescent systems to react as near to the base resin decomposition point as possible. Various temperature ranges, as well as decomposition behavior of plastics and test methods dramatically affects how readily a compound can be flame retarded. This requires flame retardants to offer a variety of temperature ranges as well as extinguishing mechanisms to meet every market demand. JJI Technologies has a committed R&D effort to span this gap and diversify its product lines to not just meet, but exceed these demands (Figure 10). There is also an ongoing effort within JJI Technologies to innovate current technologies to enhance the robustness of our JJAZZ™ processing by increasing the temperature stability.

Figure 1. Dielectric properties of 2.5µm

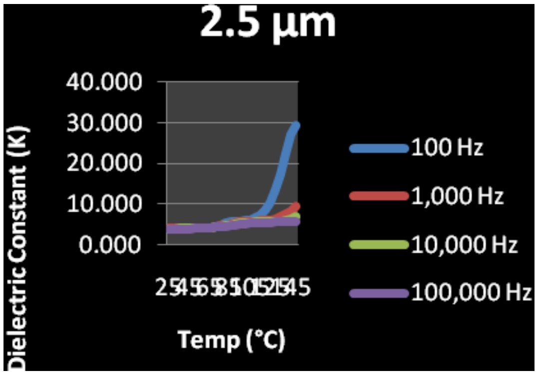


Figure 2. Dielectric properties of 6µm

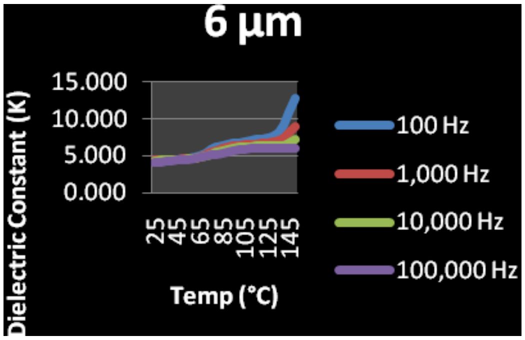


Figure 3. JJI product properties

Physical Property	JJAZZ®	*DP-110
Appearance	White Powder	White Powder
Decomposition Temp (2%, Nitrogen)	>230°C (464°F)	N/A
Activation Temp	~250°C (482°F)	~345°C (653°F)
Bulk Density	400	400
Phosphorus Content	15-17%	N/A
Nitrogen Content	>20%	N/A
pH	7.2	7.2
Specific Gravity	1.30	1.28

*DP-110 is in development

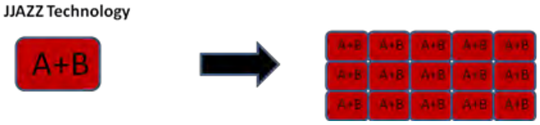
Figure 4. Conventional 2 component technology

*Gray indicates inactive

*An X indicates hydrolytically compromised

*Read and blue indicate active sites

Figure 5. JJAZZ™ single component technology



*All pairs are active

Figure 6. TGA and DSC analysis of char mechanism

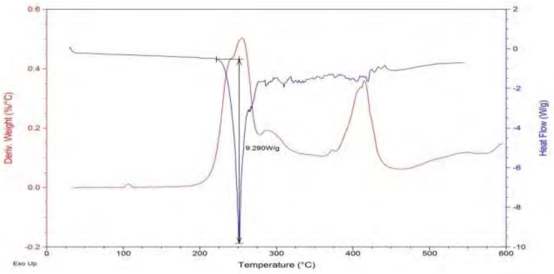


Figure 7. Performance Data

	Control	31% JJAZZ™	35% JJAZZ™	40% JJAZZ™
UL 94 1.6mm	**Fail**	**V2**	**V0**	**V0**
Specific Gravity	**0.901**	**1.04**	**1.02**	**1.03**
Hardness (Shore A)	**87.5**	**81.8**	**84.5**	**86.5**
MFI	**3.72**	**1.53**	**1.55**	**0.98**
Notch Izod	**7.857**	**1.243**	**1.101**	**1.079**
Tensile at Break	**2536**	**1906**	**1789**	**1709**
Elongation at Break	**51.21**	**66.61**	**51.52**	**30.72**
Flex Modulus	**173205**	**202987**	**217319**	**245448**

Units

- MFI (melt flow index) – (190°C/2.16kg)
- Notch Izod – (ft-lb/in)
- Tensile – (psi)
- Elongation – (%)
- Flex Modulus – (psi)

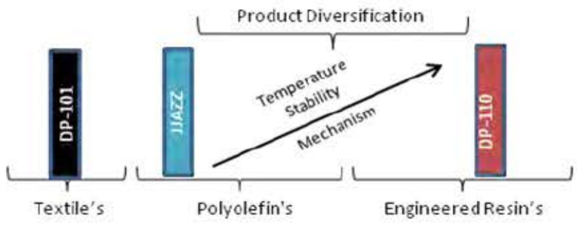
Figure 8. JJAZZ™ Processing Parameters

Die	Zone 5	Zone 4	Zone 3	Zone 2	Zone 1
380	370	340	340	350	350

Figure 9. Suggested extruder set-up

- 11 barrel extruder
- Ambient vent at barrel 6
- Side feeder at barrel 7
- Vacuum at barrel 10
- Pellet and powder in barrel 1
- A 1:2 feed ratio of powder from the rear feeder to the side feeder

Figure 10. Product Diversification



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5. Almeras, X., et al., *Structure and Morphology of an Intumescent Polypropylene Blend.* Journal of Applied Polymer Science, 2004. **93**: p. 402-411.
6. Ou. Yuxiang, *Technology of Flame Retardants.* Chemical Industry Publishing House, China. p. 205-207.

Appendix VIII: Plastics Flammability Tests: Smaller Scale Laboratory Tests

Prepared for this report by:

James Innes & Ann Innes

Flame Retardants Associates

UL 2335 and FM 4996 are the only tests for determining whether a flame retardant polymer pallet meets NFPA 13 requirements. But other tests are sometimes mentioned in the context of flame retardant plastics. Discussed below are smaller scale lab tests that often come up in discussion of fire resistant pallet testing. Some are actually more useful than others with regard to non-halogen fire resistant plastic pallets.

Testing with the Fire Propagation Apparatus

After a pallet has passed the FM 4996 test, any subsequent resin or formulation changes must be evaluated using the Fire Propagation Apparatus. If the results from this test are inconclusive, then full scale testing under the FM 4996 standard must be performed again. The Fire Propagation Apparatus is a piloted ignition open air test protocol using two 4 inch x 4 inch plaques or sheets of pallet material placed one on top of the other. The sample is exposed to external heat flux values up to 60 kW/m^2. Time to ignition is recorded along with other ignition-related data. To determine fire properties, the sample is exposed to radiant heat flux of 50 kW/m^2. Fire properties such as chemical heat release rate, mass loss rate, CO generation, and optical density of smoke are measured. This data is then used to judge if a formulation change must undergo the more costly full scale FM 4996 test protocol.

OI or LOI (Limiting Oxygen Index)

The OI or LOI test is a simple, small-scale test whose technical requirements are specified in ASTM D2863. This test measures the minimum amount of oxygen needed to support the burning process. The test is conducted in an oxygen/nitrogen atmosphere on 3 test specimens (6.5 mm wide strips of plastic) in a way that mimics candle-like burning conditions. Numerical results indicate the percentage of oxygen required to support burning of the sample. For example, a result of 28 means 28% of the oxygen/nitrogen atmosphere was oxygen and this was the amount required to just support the burning process. (Oxygen is required for burning to take place. See FR101 in the next section.) Our atmosphere on planet Earth contains about 21% oxygen. So a result in the test of 28 indicates a good degree of flame retardancy. Theoretically, such a test specimen would resist burning in a real fire scenario as atmospheric oxygen does not reach a level of 28%. See Figure App-VIII-1 for the LOI test apparatus. ["Plastic Flame Retardants: Technology and Current Developments," J. Innes & A. Innes, Rapra Review Reports, 2003. P. 7]

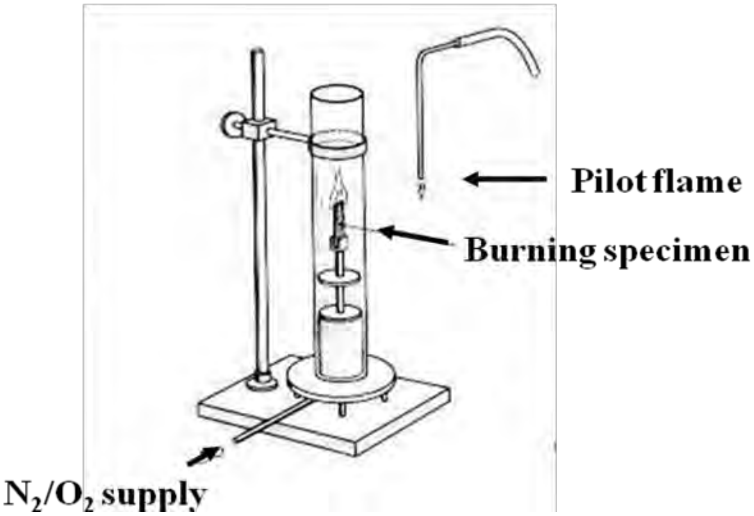

Figure App-VIII-1. LOI Test Apparatus

UL94 (Underwriters Laboratories)(Harmonized with ISO 9772, 9773)

Underwriters Laboratories UL94 test, Test for Flammability of Plastic Materials for parts in Devices and Appliances or Standard for Safety of Flammability of Plastic Materials for Parts in Devices and Appliances Testing, is perhaps the most well known flame retardant (FR) test in the industry. It has been and still is widely used for a variety of plastic materials which end up in an even wider variety of applications. This test together with UL746 A-C tests form the basis for the recognition of plastics as summarized in UL's Recognized Components Directory. UL94 applies to electrical parts, appliances, consumer and office equipment as well as other application areas *except* the use of plastics in buildings. [“Plastics Flammability Handbook,” Jurgen Troitzsch, Carl Hanser Verlag, 2004, p. 533]. The UL94 standard actually contains several test protocols. The most common involves a vertical burn method and bar-shaped test specimens (13 mm x 125 mm of varying thicknesses such as 1/8”, 1/16”, 1/32”). The test bar is suspended a specified distance above a lump of cotton while a calibrated burner flame is applied to the specimen for 10 seconds, burn time of the specimen after removal of the flame is recorded, then the flame is applied to the specimen a second time for 10 seconds, and the burn time is again recorded. This procedure is followed for a set of five test bars. Performance in the test is indicated by burn time (usually in seconds) for each specimen, total after-flame burn time for all specimens, afterglow time, and the existence of flaming drips which may ignite the cotton. See Figure App-VIII-2 for the UL94 test apparatus sketch and Table App-VIII-1 for the UL94 test classification criteria. The result is actually expressed in this protocol as UL94 V0, V1, or V1 plus the thickness of the tested specimen. [“Plastic Flame Retardants,” Innes & Innes, p. 7.]

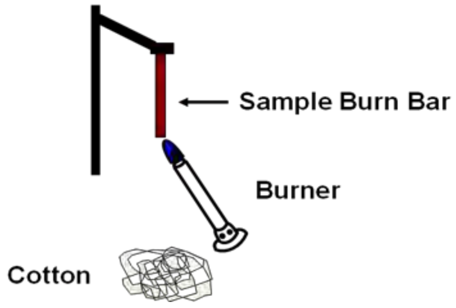

Figure App-VIII-2. UL 94 Test Apparatus

Table App-VIII-1. UL94 Materials classification (vertical burn test procedure)

Criteria	**UL94 V0**	**UL94 V1**	**UL94 V2**
Afterflame time for each individual specimen t_1 or t_2	≤ 10 s	≤ 30 s	≤ 30 s
Total afterflame (t_1 + t_2) for set of 5 specimens	≤ 50 s	≤ 250 s	≤ 250 s
Afterflame + Afterglow time (t_2 + t_3) for each specimen	≤ 30 s	≤ 60 s	≤ 60 s
Afterflame or Afterglow of any specimen up to clamp	No	No	No
Cotton indicator ignited by flaming drips	No	No	Yes

The other UL94 test protocols actually result in additional ratings including 5V (the highest flammability performance), HB (the lowest), as well as three other classifications each for horizontally burned specimens and very thin film specimens.

ASTM E2058-09 (Fire Propagation Apparatus)

ASTM's "Standard Test methods for Measurement of Synthetic Polymer Material Flammability Using a Fire Propagation Apparatus" actually uses flames from the burning material itself to characterize fire behavior. Laboratory measurements include heat release taken during upward fire propagation and burning on a vertical test specimen in specific atmospheres (normal air, oxygen rich, and/or oxygen partially depleted). Other measurements include time to ignition, chemical and convective heat release rates for horizontal specimens, mass loss rate and effective heat of combustion. [ASTM E2058-09]. This is the same apparatus referred to for testing the effects of any formulation changes to an FM 4996-approved pallet described above.

ASTM E1354 (ISO 5660) Cone Calorimeter

Unlike some of the above long-lived lab tests, the cone calorimeter is a comparatively newer test used to evaluate and measure rate of heat release of a burning test specimen. In ASTM 1354 (ISO 5660) Standard Test Method for Heat and Visible Smoke Release Rates for Materials and Products Using an Oxygen Consumption Cone Calorimeter, peak and total heat release rates as well as combustion gas composition are assessed in this test and used to characterize the tested materials. See Figure App-VIII-3 for a sketch of the apparatus.

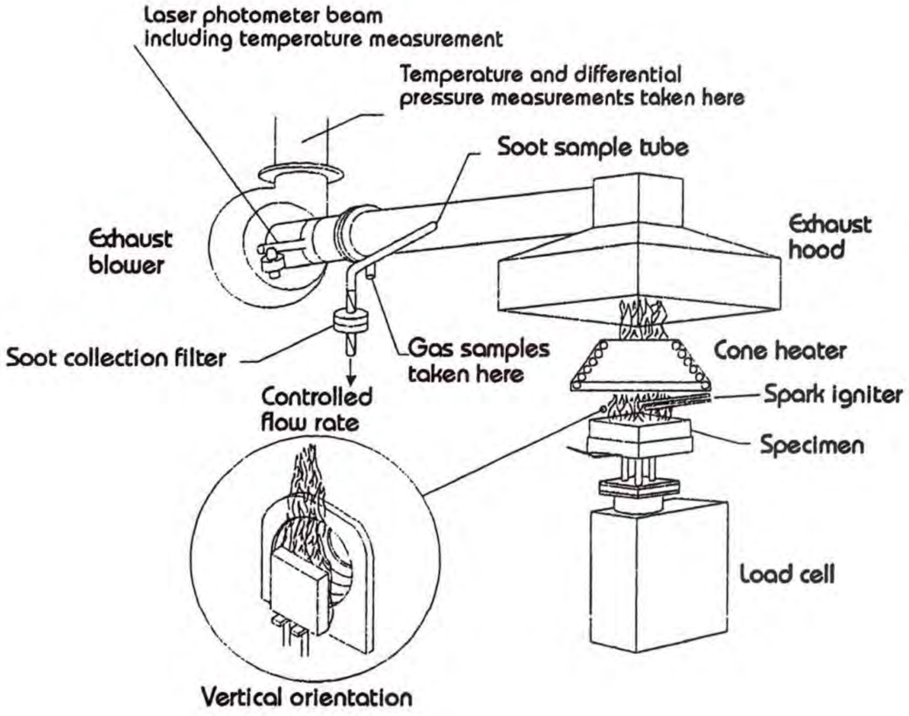

Figure App-VIII-3. Cone Calorimeter Apparatus sketch (Drawing by NIST) (23)

The actual test report includes a total of 24 reported items such as Time to Sustained Flaming (seconds), Heat Release Rate per unit area curve (kW/ms^2), Peak and Average Heat Release Rates for 60 seconds, 180 seconds, and 300 seconds after ignition (kW/m^2), Sample Mass Loss (kg/m^2), Smoke Obscuration (average extinction area m^2/kg), and if properly equipped measurements of other combustion gases are also included. [ASTM E1354-04a]

In the authors' opinion, the cone calorimeter and the FM heat release or fire propagation apparatus are the best and possibly the only good test to use in screening a formulation for application in FR plastic pallet. The ultimate requirement in both the FM and UL idle pallet flammability testing is to prove the FR plastic pallet is "like wood" or better. The smaller lab tests like UL94, LOI, etc, are all designed to indicate flame out, not continued burning "like wood". In the cone calorimeter, when wood is evaluated the peak rate of heat release is between 300-325 kW/m^2 at 50 kW incident heat. This value provides a benchmark for evaluation of any FR plastic formulation in comparison to wood.

Readers are cautioned that when evaluating in the cone, one flame retardant system can not necessarily be compared to a different flame retardant system. Allowances must be made for differences in fire retardancy mechanism.

The FM Fire Propagation Apparatus could also be used for screening purposes. However, a baseline must be established and the authors have been unable to locate such a baseline in the available literature.

Appendix IX

GREEN SCREEN ALTERNATIVES ASSESSMENTS FOR NINE FLAME RETARDANTS

November 30, 2010

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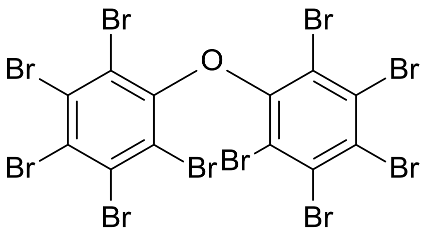
APPENDIX IXB: GREEN SCREEN FOR DECABROMODIPHENYL ETHER (CAS #1163-19-5)[2]

Also Called: 1,1'-Oxybis(2,3,4,5,6-pentabromobenzene), 1-06-00-00108 (Beilstein Handbook Reference), AFR 1021, AI3-27894, Adine 505, BDE 209, BDE-209, BR 55N, BRN 2188438, Berkflam B 10E, Bis(pentabromophenyl) ether, Bis(pentabromophenyl)ether, Bromkal 82-0DE, Bromkal 83-10DE, CCRIS 1421, Caliban F/R-P 39P, DB 10, DB 101, DB 102, DE 83, DP 10F, De 83R, Decabrom, Decabromdiphenyl oxide, Decabromobiphenyl ether, Decabromobiphenyl oxide, Decabromodiphenyl ether, Decabromodiphenyl oxide, Decabromophenyl ether, EB 10, EB 10FP, EB 10W, EB 10WS, EBR 700, EINECS 214-604-9, Ether, decabromodiphenyl, F/R-P 53, FR 10, FR 10 (ether), FR 300, FR 300BA, FR-PE, FR-PE(H), FRP 53, Fire Cut 83D, Flame Cut 110R, Flame Cut Br 100, HSDB 2911, NCI-C55287, NSC 82553, Nonnen DP 10, Nonnen DP 10(F), PBED 209, Pentabromophenyl ether, Planelon DB, Planelon DB 100, Planelon DB 101, Plasafety EB 10, Plasafety EBR 700, Saytex 102, Saytex 102E, Tardex 100

Chemical Structure of Decabromodiphenyl Ether:



For Inorganic Chemicals:
Define Form & Physiochemical Properties

1. Particle size (e.g. silica of respirable size) – n/a
2. Structure (e.g. amorphous vs. crystalline) – microcrystalline (NTP 1986)
3. Mobility (e.g. Water solubility, volatility) – 0.1 µg/L at 25˚C (Leisewitz 2000)

Identify Applications/Functional Uses: Flame retardant

Green Screen Rating[3]: Decabromodiphenyl ether was assigned a Benchmark Score of 1 based on a very High persistence (P) rating and High toxicity ratings for both acute (AA) and chronic (CA) aquatic toxicity (1c).

Green Screen (Version 1) Levels of Concern for Decabromodiphenyl Ether														
Human – Tier 1					**Human – Tier 2**				**Eco**		**Fate**		**Physical**	
C	**M**	**R/D**	**ED**	**N**	**AT**	**Cr**	**Sn**	**ST**	**AA**	**CA**	**P**	**B**	**Ex**	**F**
M	**L**	**M**	**M**	**M**	**L**	**M**	**L**	**M**	**H**	**H**	**vH**	**M**	nd	**L**

*Endpoints in italics were assigned using estimated values and professional judgment (Structure Activity Relationships).

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[2] CPA recommends independent third-party validation of all Green Screen assessments. No independent third-party validation has been done for this assessment . Companies may not make marketing claims based on a Green Screen assessment that has not undergone an independent validation.

[3] For inorganic chemicals with low human and ecotoxicity across all hazard endpoints and low bioaccumulation, persistence alone will not be deemed problematic. Inorganic chemicals that are only persistent will be evaluated under the criteria for Benchmark 4.

Transformation Products and Ratings:
Identify relevant fate and transformation products (i.e., dissociation products, transformation products, valence states) **and/or moieties of concern**[4]

Life Cycle Stage	Transformation Pathway	Transformation Products	CAS #	Green Screen Rating
End of Life	UV Degradation	Low brominated diphenyl oxides	Multiple	n/a
End of Life	UV Degradation	PentaBDE	32534-81-9	PBT (CPA 2009)
End of Life	Combustion	Dioxin	1746-01-6	PBT, Carcinogen, Reproductive/Developmental Toxicant, Neurotoxicant, Endocrine Disruptor (CPA 2009)
End of Life	Combustion	Furan	110-00-9	Carcinogen (CPA 2009)
End of Life	Combustion	Carbon dioxide	124-38-9	Not present on the Red List of Chemicals (CPA 2009)
End of Life	Combustion	Carbon monoxide	630-08-0	Reproductive/Developmental Toxicant, Neurotoxicant (CPA 2009)
End of Life	Combustion	Hydrogen bromide	10035-10-6	Not present on the Red List of Chemicals (CPA 2009)

*The above transformation products were screened against the CPA‘s table of Red List chemicals.

Introduction

Decabromodiphenyl oxide (―DecaBDE" or ―Deca") is an additive flame retardant used in a wide range of polymers including high impact polystyrene, engineering thermoplastics, and textile coating (Leieswitz 2000). DecaBDE has low water solubility (0.1 µg/L at 25˚C) and a log K_{ow} of > 5, which indicates a tendency to bioaccumulate. DecaBDE targets the liver, kidneys, spleen, and fat (Leieswitz 2000). The general population may be exposed to decaBDE via inhalation of ambient air, ingestion of fish, and dermal contact with products such as television or computer enclosures or textiles containing decaBDE (HSDB 2010). Studies have shown that all polybrominated diphenyl ethers (PBDEs) bioaccumulate in the environment and that the accumulation is inversely proportional to the degree of bromination (Darnerud 2001). Once in the environment, PBDEs biomagnify in the food chain. Because PBDEs accumulate in fat tissue, high levels of these compounds have been found in fatty fish.

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[4] A moiety is a discrete chemical entity that is a constituent part or component of a substance. A moiety of concern is often the parent substance itself for organic compounds. For inorganic compounds, the moiety of concern is typically a dissociated component of the substance or a transformation product.

DecaBDE is most commonly used as a flame retardant. It is the most common of all polybrominated diphenyl ethers (NAS 2000). The major impurities are isomers of nonabromodiphenyl oxide and octabromodiphenyl oxide. The flame retardant mixture consists of approximately of 66-75% decaBDE and 25-33% antimony trioxide, a synergist (NAS 2000).

Recently, several U.S. states have placed bans on the manufacture or distribution of products containing decaBDE (OECD 2008). The European Union has requested a voluntary reduction program of decaBDE by manufacturers. Under An Act to Clarify Maine‘s Phaseout of Polybrominated Diphenyl Ethers (Public Laws 2009, chapter 610 [PL 2009, c. 610]), the Maine Department of Environmental Protection (DEP) is currently prohibiting the sale of shipping pallets containing decaBDE unless the pallet is made from recycled shipping pallets or unless an exemption has been granted by the Commissioner of Environmental Protection. The act additionally prohibits the replacement of decaBDE in pallets with other brominated or chlorinated flame retardants. DecaBDE has also been banned from being used in the manufacturing of mattresses and home furniture in Maine and California (OECD 2008).

Human Health – Tier 1

Carcinogenicity (C) Score (H, M or L): M

DecaBDE was assigned a score of Moderate for carcinogenicity based on evidence suggesting the chemical may be carcinogenic in humans and animals.

- DecaBDE has been assigned the following EU risk phrase: R40- Limited evidence of a carcinogenic effect (Physchem 2003).
- Feeding 3,500 to 7,000 mg/kg-bw to mice and 1,200 to 2,400 mg/kg-bw to rats suggests an elevated risk of cancer in the liver, pancreas, thyroid gland as well as an increased risk of leukemia (Leisewitz 2000).
- There is a reported increase in incidence of gullet cancer, rectum carcinoma, and duodenal cancer in decaBDE-exposed workers. However, due to contradictory results, the NTP and IARC have yet to classify decaBDE for carcinogenicity (Leisewitz 2000).
- Groups (50/sex/dose) of F344/N rats and B6C3F1 mice that were fed decaBDE (94–97% pure) at dietary concentrations of 0, 25,000, or 50,000 ppm for 103 weeks (equivalent to 1120, 1200, and 2240 mg/kg-d in male rats; 1120, 1200, and 2550 mg/kg-d in female rats; 3200, 3760, and 6650 mg/kg-d in male mice; and 3200, 3760, and 7780 mg/kg-d in female mice, respectively) Incidences of liver neoplastic nodules were significantly increased in low- and high-dose male rats (7/50 and 15/49, respectively, compared to 1/50 in controls) and high-dose female rats (9/50 compared to 1/50 and 3/49 in control and low-dose groups, respectively); this lesion appeared to be compound related. Incidence of hepatocellular carcinomas was low in all rat groups and apparently not compound related. There was a positive trend in mononuclear cell leukemia in male rats (30/50 controls, 33/50 low-dose rats, 35/50 high-dose rats), but the increase was marginal and not considered to be biologically significant because of the unusually high incidence in controls. A significant positive trend and marginally

greater incidence of acinar cell adenomas in the pancreas of high-dose male rats were also observed, but this lesion was considered to not be compound related. Hepatocellular adenomas or carcinomas (combined) were significantly increased in low- and high-dose male mice (8/50 controls, 22/50 low-dose mice, 18/50 high-dose mice). The incidence of hepatocellular carcinomas alone was significantly elevated in male mice in the low-dose group, but not in the high-dose group, as compared with controls. Thyroid gland follicular cell adenomas or carcinomas (combined) were marginally, but not significantly increased in male mice (0/50 controls, 4/50 low-dose mice, 3/50 high-dose mice). The possible significance of this finding was strengthened by increased incidences of follicular cell hyperplasia in the male mice (2/50 controls, 10/50 low-dose mice, 19/50 high-dose mice), but was weakened by increased mortality in control animals. There was no evidence of carcinogenicity in the female mice at either dose. The study concluded that there was –some evidence of carcinogenicity” for male and female rats based on significantly increased incidences of neoplastic nodules of the liver, and –equivocal evidence of carcinogenicity” for male mice based on a significantly increased incidence of hepatocellular tumors in only the low-dose group and non-statistically significant increases in thyroid follicular cell tumors in both dose groups. The conclusion of –some evidence of carcinogenicity” in rats appears to be based on the finding that the only chemical related effect was benign liver neoplasms. The conclusion of –equivocal evidence of carcinogenicity” in male mice appears to be based on the interpretation that the increases in liver and thyroid tumors are marginal and chemical related (NTP 1986).

Mutagenicity (M) and Genotoxicity Score (H, M or L): L

DecaBDE was assigned a score of Low for mutagenicity based on negative results from several genotoxicity assays.

- DecaBDE tested negative for mutagenicity in *Salmonella typhimurium* tester strains TA 100, TA 1535, TA 1537, and TA 98 at concentrations of 0, 100, 333, 1,000, 3,333, and 10,000 µg/plate with and without metabolic activation (NTP 1986).
- DecaBDE did not induce mutations in mouse L5178Y lymphoma cells with and without S9 at doses of 7, 8, 9, and 10 µg/mL (NTP 1986).
- DecaBDE did not induce sister-chromatid exchanges in Chinese hamster ovary cells both in the presence and absence of S9 at doses of 50, 100, 250, and 500 µg/mL (NTP 1986).
- DecaBDE did not induce chromosomal aberrations in Chinese hamster ovary cells at concentrations of 50, 100, 250, and 500 µg/mL in the presence and absence of S9 (NTP 1986).

Reproductive (R) and Developmental (D) Toxicity Score (H, M or L): M

DecaBDE was assigned a score of Moderate for reproductive and developmental toxicity based on the following risk phrase- R63.

- DecaBDE has been assigned the following EU risk phrase: R63- Possible risk of harm to the unborn child (Lookchem 2008).

- Male (10-15/dose) and female (20-30/dose) Sprague-Dawley rats were administered decaBDE (77.4% pure) daily for 60 days pre-mating, mating, gestation, and lactation for a total of approximately 115 days. Doses were 0, 3, 30, and 100 mg/kg. The reproductive NOAEL was 100 mg/kg (NAS 2000).
- Female rats (strain and number of animals not reported) were administered decaBDE (77.4% pure) at doses of 0, 10, 100, and 1,000 mg/kg on gestation days 6 through 15 via gavage in corn oil. No maternal toxicity or fetal malformations were observed. Subcutaneous edema and delayed skull ossification in pups was observed at 1,000 mg/kg. The maternal NOAEL was 1,000 mg/kg. The fetal NOAEL was 100 mg/kg and the LOAEL was 1,000 mg/kg (NAS 2000).
- Sprague-Dawley rats (25 mated females per dose group) were administered decaBDE in corn oil by gavage at doses of 0, 100, 300, or 1,000 mg/kg-day during gestation days 0 through 19. Dams were sacrificed on day 20 of gestation, and liver weights, gravid uterine weights, and the number of corpora lutea, implants, fetuses, and resorptions were recorded. The placenta and fetuses were examined for gross abnormalities, and histologic examinations were performed. All dams survived decaBDE treatment until scheduled sacrifice. There were no adverse treatment-related effects observed in maternal clinical findings, body weight, or body-weight gain. Although a slight but statistically significant increase in food consumption was observed at 1,000 mg/kg-day at time intervals up to day 12 of gestation, the authors did not consider this indicative of an adverse effect of treatment. No statistically significant differences were observed in maternal absolute or relative liver weights between treatment and control groups. At necropsy, gross examination of the dams revealed no adverse effect of treatment with decaBDE. Number of dams with viable fetuses, mean number of corpora lutea, number of implantation sites, percent preimplantation loss per dam, number of viable fetuses, and gravid uterine weights were not adversely affected by decaBDE treatment. A statistically significant increase in the mean number of early resorptions per dam was observed in the 1,000 mg/kg-day group compared to controls. Based on the lack of a consistent dose response for this effect (the mean number of early resorptions per dam was 0.6, 0.6, 0.5, and 1.4 at 0, 100, 300, and 1,000 mg/kg-day, respectively), lack of a statistically significant positive trend associated with the effect, and the historically high incidence of this effect (0.5–1.4) for the laboratory, these effects are not considered to be of toxicological significance. Examination of the results indicated a marginal increase in the postimplantation loss/dam of 7 and 9% at 300 and 1,000 mg/kg-day, respectively, compared with 4% in controls and at 100 mg/kg-day. However, this effect was not associated with a statistically significant positive trend. A slight, but statistically not significant, decrease in the percentage of viable fetuses per implant was seen (96, 96, 93, and 91% in the control, 100, 300, and 1,000 mg/kg-day groups, respectively). Fetal body weights, crown-rump ratio, and fetal sex ratio were not different between treatment and control groups. No adverse decaBDE treatment-related effects were identified during fetal external, skeletal, or visceral examinations. DecaBDE treatment, therefore, did not produce any evidence of maternal or developmental toxicity up to the highest dose tested of 1,000 mg/kg-day. The NOAEL for maternal and developmental toxicity in this study was 1,000 mg/kg-day, the highest dose tested (IRIS 2008).

Endocrine Disruption (ED) Score (H, M or L): M

DecaBDE was assigned a score of Moderate for endocrine disruption based on the chemical being listed as a potential endocrine disruptor.

- DecaBDE is listed as a potential endocrine disruptor on the EU Priority List of Suspected Endocrine Disruptors.
- DecaBDE is not listed as a potential endocrine disruptor on the OSPAR List of Chemicals of Possible Concern.
- DecaBDE is listed as a potential endocrine disruptor on the Red List of Chemicals (CPA 2009).
- There is suggestive evidence of hypothyroidism in a small number of workers occupationally exposed to decaBDE (ADSTR 2004).
- Long-Evans female rats (eight animals/dose group) were orally administered decaBDE (>98% purity) in corn oil at doses of 0, 0.3, 1, 3, 10, 30, 60, or 100 mg/kg-day for 4 consecutive days. Body weights were recorded and dosing volumes adjusted daily. Animals were sacrificed 1 day after the last dose. Serum total thyroxine (T4) and triiodothyronine (T3), serum thyroid stimulating hormone (TSH), and hepatic enzyme activities (EROD, a marker for CYP-1A1; PROD, a marker for CYP-2B1; and T4-uridine diphosphate glucuronyl transferase [T4-UDPGT]) were measured. Short-term treatment with decaBDE did not cause any visible signs of toxicity or any effects on body-weight gain or liver-to-body-weight ratios at any dose level. DecaBDE (up to 100 mg/kg-day) had no effect on serum T4, T3, or TSH concentration or on hepatic UDPGT activity. Based on these observations, the highest dose of 100 mg/kg-day is identified as the NOAEL (IRIS 2008).

Neurotoxicity (N) Score (H, M or L): M

DecaBDE was assigned a score of Moderate for neurotoxicity based on beings listed as a potential neurotoxicant on the Red List of Chemicals and based on an animal study that suggests decaBDE caused a decrease in activity.

- Not classified as a developmental neurotoxicant (Grandjean and Landrigan 2006).
- DecaBDE is listed as a potential neurotoxicant on the Red List of Chemicals (CPA 2009).
- The neurotoxic effects of decaBDE on spontaneous motor behavior of NMRI male mice were investigated in adult animals exposed to a single oral dose as neonates. Uptake of radiolabel by the brain of the neonatal mice orally administered 14C-labeled decaBDE on PND 3, 10, or 19 (i.e., at different stages of neonatal mouse brain development) was also measured to determine if there were age-related differences in tissue toxicokinetics that might correlate with the neurodevelopmental effects evaluated. In this behavioral study, 3-day-old and 19-day-old male mice were given a single dose of 0, 2.22, or 20.1 mg/kg body weight decaBDE (purity estimated to be >99%) in a 20% (weight/weight) emulsion vehicle of egg lecithin-peanut oil and water. Ten-day-old mice received 0, 1.34, 13.4, or 20.1 mg/kg. The spontaneous behavior test (measuring locomotion, rearing, and total activity) was conducted in 10 mice randomly selected from the litters in each treatment group at 2, 4, and 6 months of age. Treatment with decaBDE caused no clinical signs of toxicity at any time during the experimental period. Body weight and body-weight gain were not significantly different

between decaBDE- and vehicle-treated mice in the three different age groups. Control mice treated on PND 3, 10, or 19 exhibited normal habituation profiles. Pair-wise testing between adult mice exposed to 20.1 mg/kg on PND 3 and control groups indicated significant changes in all three spontaneous behavior variables at 2, 4, and 6 months of age. For the first 20 minutes, mice receiving 20.1 mg/kg displayed significantly less activity for locomotion, rearing, and total activity compared with controls. During the third 20-minute period, exposure of mice to 20.1 mg/kg on PND 3 caused significantly more activity for locomotion, rearing, and total activity than the controls at 2, 4, and 6 months. The only effect noted in mice exposed to 2.22 mg/kg was a significant decrease in total activity in the first 20-minute test period compared with the controls at 2 months of age. However, total activity returned to control level during the third 20-minute period. The lower dose of 2.22 mg/kg did not elicit any significant differences in these three variables compared with controls at 4 months of age. Lower activity was observed at 2.22 mg/kg during the first 20-minute period for the rearing variable at 6 months of age compared with controls, again returning to control level during the third 20-minute period. Mice exposed neonatally up to 20.1 mg on either PND 10 or 19 did not show any significant differences in any of the variables after 2, 4, or 6 months compared with controls. The authors indicated that the absence of effects on spontaneous activity in mice treated on PNDs 10 and 19 suggests that there is a critical window for the induction of the observed behavioral disturbances. The NOAEL in this study was 2.22 mg/kg, and the LOAEL was 20.1 mg/kg for significant changes in spontaneous motor behavior and decreased habituation capability for locomotion, rearing, and total activity, worsening with increasing age (IRIS 2008).

Human Health – Tier 2

Acute Mammalian (AT) Toxicity Score (H, M or L): L

DecaBDE was assigned a score of Low for acute mammalian toxicity based on oral and dermal LD_{50} values greater than 2,000 mg/kg-bw. Data is from three different routes of exposure in two different species of animals.

- DecaBDE has low acute oral toxicity because it is poorly absorbed from the gastrointestinal tract (NAS 2000).
- *Oral*: An LD_{50} of > 2,000 mg/kg was determined in the rat (ESIS 2000).
- *Oral*: An LD_{50} of > 5,000 mg/kg was determined in the rat (ESIS 2000).
- *Dermal*: An LD_{50} of > 2,000 mg/kg was determined in the rabbit (ESIS 2000).
- *Inhalation*: An LC_{50} of > 48.2 mg/L was determined in the rat (ESIS 2000).
- *Inhalation*: No deaths occurred in groups of 5 male and 5 female rats chamber-exposed to decaBDE dust mixture at concentrations as high as 48,200 mg/m^3 for 1 hour and observed the following 14 days (ATSDR 2004).

Corrosion/ Irritation (Skin/ Eye) (Cr) Score (H, M or L): M

DecaBDE was assigned a score of Moderate for corrosion and irritation based on the following risk phrases: R36, R37, R38.

- DecaBDE has been assigned the following EU risk phrases: R36- Irritating to eyes, R37- Irritating to respiratory tract, R38- Irritating to skin (Physchem 2003).
- Although animal studies have shown decaBDE to not be corrosive or irritating, occupational reports have suggested the substance produces skin and eye irritation (Leisewitz 2000).
- *Dermal*: DecaBDE caused essentially no dermal response in rabbits when applied as a dry solid (500 mg) to intact shaved skin under occluded conditions for 24 hours, and a slight erythematous and edematous response when similarly applied to abraded skin. Repeated application of dry solid decaBDE (500 mg) to intact skin of rabbits for 5 days/week for 2 weeks or to abraded skin for 3 days also did not alter their dermal responses (NAS 2000).
- *Dermal*: An acnegenesis study was performed in which 0.1 mL of 0.1%, 1%, 10%, or 100% decaBDE (0.40 mg/kg) in chloroform was rubbed into the external ear canal of four rabbits/dose level once a day, 5 days/week for 4 weeks. Observations made prior to the initial dose and after 7, 14, 21, and 28 days of dosing showed slight erythema, epidermal sloughing and scaling (effect levels not specified), but no clear indication of chloracne (a slight response was observed in one animal at the 10% concentration on day 28). Gross necropsy showed no treatment-related systemic effects. Other studies similarly reported that a 10% chloroform solution of decaBDE caused slight erythema and exfoliation, and no indication of chloracne, when applied to the ear of rabbits for 28 days. Other industry studies also found that 10% decaBDE in chloroform did not induce chloracne in rabbits (NAS 2000).
- *Ocular*: Ocular exposure to dry solid decaBDE caused transient conjunctival irritation in washed and unwashed rabbit eyes. Instillation of decaBDE (100 mg/eye) into the eye caused very slight conjunctival redness and chemosis and slight or moderate discharge in some rabbits, but the investigators concluded that the effects were not serious enough to be considered primary eye irritation. Other studies similarly reported that decaBDE did not cause primary eye irritation when instilled once (100 mg/eye) into the eye of rabbits (NAS 2000).
- *Ocular*: Rats (strain and number not reported) that were chamber-exposed to decaBDE dust at concentrations of 48,200 mg/m3 for one hour showed signs of eye squint, erythema, and/or ocular discharge (ADSTR 2004).

Sensitization (Sn) Score (Skin and Respiratory) (H, M or L): L

DecaBDE was assigned a score of Low for sensitization based on negative results from human and animal studies.

- *Dermal*: DecaBDE does not appear to be a primary irritant based on observations from a skin sensitization study in humans and dermal irritation and acnegenesis studies in animals. A human skin sensitization study was conducted in which 0.03 mL of a 5% suspension of commercial decaBDE in petrolatum (0.02 mg/kg) was applied via patch to the skin of 50 subjects three times per week for 3 weeks. Commercial decaBDE was a mixture that contained 77.4% decaBDE, 21.8% nonaBDE, and 0.8% octoBDE. The dermal applications did not result in skin sensitization reactions during the sensitizing period or on challenge 2 weeks after the last application. Skin irritation, attributed to the stringency of the test procedure by the investigators, occurred in 9 of the 50 subjects (14/450 total applications; 11 of the reactions were classified as very slight and 3 as mild erythema) (NAS 2000).

Systemic/ Organ (ST) Toxicity Score (includes organ effects and immunotoxicity) (H, M or L): M

DecaBDE was assigned a score of Moderate for systemic toxicity based on animal studies and the following risk phrases: R20, R21, R22, R48/20.

- DecaBDE has been assigned the following EU risk phrases: R20- Harmful by inhalation, R21- Harmful in contact with skin, R22- Harmful if swallowed (Physchem 2003) and R48/20- Danger of serious damage to health by prolonged exposure and harmful by inhalation (Lookchem 2008).
- DecaBDE will accumulate in the liver, kidneys, and fat tissue of animals (Leisewitz 2000).
- Rats (strain, sex, and number of animals not reported) were exposed to decaBDE at concentrations of 2,000 or 48,000 mg/m^3 via inhalation for 1 hour and then observed for 14 days. No deaths or effects on body weight were observed however, dyspnea and ocular porphyrin discharge were observed at both concentration levels and eye squint was observed in the high concentration level only (NAS 2000).
- Male Sprague-Dawley rats (5/dose) were administered oral doses of decaBDE (77.4% pure) at 0, 8, 80, and 800 mg/kg per day for 30 days. Clinical symptoms included thyroid hyperplasia at the 80 and 800 mg/kg dose levels, increased liver weight at 80 mg/kg, increased liver weight and pathology at 800 mg/kg, and renal tubular degeneration at 800 mg/kg. A NOAEL of 8 mg/kg-day and LOAEL of 80 mg/kg-day was assigned (NAS 2000).
- Male and female rats (10/dose, strain not reported) were administered decaBDE (purity not reported) orally in doses of 0, 7.4, or 74 mg/kg-day for 28 days. No histological liver or thyroid changes were observed and the NOAEL was established to be 74 mg/kg-day (NAS 2000).
- In a 2 year oral study, male and female Sprague-Dawley rats (25/dose) were administered decaBDE (77.4% pure) at concentrations of 0, 0.01, 0.1, or 1 mg/kg-day. No adverse effects were observed and the NOAEL was established to be 1 mg/kg-day (NAS 2000).
- Male and female F344/N rats (5/sex/dose) were fed diets containing 0, 5,000, 10,000, 20,000, 50,000, or 100,000 ppm decaBDE (99% purity) for 14 days. The corresponding estimated average daily doses were 0, 472, 928, 1,846, 4,569, or 9,326 mg/kg-day in male rats and 0, 538, 1,061, 2,137, 5,323, or 10,853 mg/kg-day in female rats. No mortality was observed in the rats during the course of the study. Exposure to decaBDE did not cause any clinical signs of toxicity or adversely affect the final mean body weights. Gross pathological effects were not noted in any animal at any dose level. The results of this study indicated a NOAEL of 9,326 mg/kg-day in male rats and 10,853 mg/kg-day in female rats (NTP 1986).
- The subchronic effects of decaBDE (97–99% purity) on rats were investigated in a 13-week study. Groups of F344/N rats (10/sex/dose) were administered decaBDE in the diet at concentrations of 0, 3,100, 6,200, 12,500, 25,000, or 50,000 ppm for 13 weeks. The corresponding estimated average daily doses were

0, 191, 372, 781, 1,536, or 3,066 mg/kg-day in male rats and 0, 238, 504, 967, 1,955, or 3,944 mg/kg-day in female rats. A necropsy was performed on all animals, including those killed in extremis, with the exception of those excessively autolyzed or cannibalized. Histologic examination was performed on major organs and tissues from control and high-dose groups. No mortality was observed in rats fed decaBDE, and no clinical signs of toxicity were noted. Compound-related changes in body weight and feed consumption were not observed, and no gross or macroscopic pathological effects were noted in any animal examined. The results indicate a NOAEL of 3,066 mg/kg-day in male rats and 3,944 mg/kg-day in female rats (NTP 1986).

- Male and female B6C3F1 mice (5/sex/dose) were fed diets containing 0, 5,000, 10,000, 20,000, 50,000, or 100,000 ppm decaBDE (99% purity) for 14 days. The estimated average daily doses were 0, 1,027, 2,143, 4,246, 10,536, or 20,994 mg/kg-day in male mice and 0, 1,146, 2,286, 4,627, 11,348, or 23,077 mg/kg-day in female mice. Necropsy was performed at the end of the exposure period, and several organs and tissues were examined histologically. Exposure to decaBDE up to 20,994 mg/kg-day in males and 23,077 mg/kg-day in females showed no effects on survival or body weight, and there were no clinical signs of toxicity. No compound-related gross pathological effects were noted in any animal in any group. The results of this study indicate a NOAEL of 20,994 mg/kg-day in male mice and 23,077 mg/kg-day in female mice (NTP 1986).
- B6C3F1 mice (10/sex/dose) were fed diets containing 0, 3,100, 6,300, 12,500, 25,000, or 50,000 ppm decaBDE (97–99% purity) for 13 weeks. The corresponding estimated average daily doses were 0, 666, 1,355, 2,659, 5,278, or 10,233 mg/kg-day in males and 0, 702, 1,437, 2,899, 5,687, or 11,566 mg/kg-day in females. Necropsy was performed on all animals, including those killed in extremis, with the exception of those excessively autolyzed or cannibalized. Histologic examination was performed on the organs and tissues from control and high-dose groups. Only one male and one female mouse fed 12,500 ppm died in the course of the study. There were no clinical signs of toxicity, and no compound-related effects on body weight and feed consumption were observed. No gross or macroscopic pathological effects were noted in any animal at any dose. The results of this study indicated a NOAEL of 10,233 mg/kg-day in males and 11,566 mg/kg-day in females (NTP 1986).

Ecotoxicity

Acute Aquatic (AA) Toxicity Score (H, M or L): H

DecaBDE was assigned a score of High for acute aquatic toxicity based on L/EC$_{50}$ values less than 1 mg/L.

- An LC$_{50}$ of > 500 mg/L was identified in killifish (freshwater fish, 48 hour) (ESIS 2000).
- ECOSAR – DecaBDE is designated to the neutral organics ECOSAR class. The estimated L/EC$_{50}$ values are 9.4×10^{-7} mg/L (fish, 96 hr), 2.36×10^{-6} mg/L (daphnid, 48 hr), and 9.05×10^{-5} mg/L (algae, 96 hr) (U.S. EPA 2009).
- An EC$_{50}$ of > 1 mg/L was identified in algae (ESIS 2000).

Chronic Aquatic (CA) Toxicity Score (H, M or L): H
DecaBDE was assigned a score of High for chronic aquatic toxicity based on ChV values less than 0.1 mg/L.

- DecaBDE has been assigned the following EU risk phrase: R50/53- Very toxic to aquatic organisms, may cause long term effects in the aquatic environment (Lookchem 2008).
- ECOSAR – The estimated ChV values are $6.06\text{x}10^{-7}$ mg/L (fish, 96 hr) and $1.36\text{x}10^{-6}$ mg/L (daphnid) (U.S. EPA 2009).

Environmental Fate

Persistence (P) Score (vH, H, M, or L): vH
DecaBDE was assigned a score of very High for persistence based on the chemical not being readily biodegradable and a half life in soil greater than 180 days and a half life in water greater than 60 days.

- BIOWIN predicts decaBDE will not readily biodegrade. STP removal expected using BIOWIN/EPA Draft Method results indicate 94.04% total removal, with 0.78% due to biodegradation. Fugacity modeling predicts 95.6% partitioning to soil with a half-life of 360 days, and 4.26% partitioning to water with a half-life of 180 days (U.S. EPA 2010).

Bioaccumulation (B) Score (vH, H, M, or L): M
DecaBDE was assigned a score of Moderate for bioaccumulation based on a BAF less than 500, and a log K_{ow} greater than 5, and degradation products that are likely to bioaccumulate.

- BCFBAF predicts a bioaccumulation factor (BAF) of 6.929 and a log K_{ow} of 12.11 (U.S. EPA 2010).

Physical Properties

Explosivity (Ex) Hazard Rating (H, M or L): nd

- No relevant data were identified for DecaBDE.

Flammability (F) Hazard Rating (H, M or L): L
DecaBDE was assigned a score of Low for flammability because no basis for concern was identified.

- DecaBDE is not flammable (ESIS 2000).

EPI Suite Results for Decabromodiphenyl Ether:

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CAS Number: 1163-19-5
SMILES : O(c(c(c(c(c1Br)Br)Br)Br)c1Br)c(c(c(c(c2Br)Br)Br)Br)c2Br
CHEM   : Benzene, 1,1 -oxybis[2,3,4,5,6-pentabromo-
MOL FOR: C12 Br10 O1
MOL WT : 959.17
------------------------------ EPI SUMMARY (v4.00) --------------------------
 Physical Property Inputs:
    Log Kow (octanol-water):   ------
    Boiling Point (deg C)  :   ------
    Melting Point (deg C)  :   ------
    Vapor Pressure (mm Hg) :   ------
    Water Solubility (mg/L):   ------
    Henry LC (atm-m3/mole) :   ------

 Log Octanol-Water Partition Coef (SRC):
    Log Kow (KOWWIN v1.67 estimate) =  12.11

Boiling Pt, Melting Pt, Vapor Pressure Estimations (MPBPVP v1.43):
    Boiling Pt (deg C):  589.71  (Adapted Stein & Brown method)
    Melting Pt (deg C):  254.50  (Mean or Weighted MP)
    VP(mm Hg,25 deg C):  4.67E-012  (Modified Grain method)
    VP (Pa, 25 deg C) :  6.23E-010  (Modified Grain method)
    MP  (exp database):  295 deg C
    BP  (exp database):  530 deg C
    Subcooled liquid VP: 4.74E-009 mm Hg (25 deg C, Mod-Grain method)
                       : 6.32E-007 Pa (25 deg C, Mod-Grain method)

 Water Solubility Estimate from Log Kow (WSKOW v1.41):
    Water Solubility at 25 deg C (mg/L):  2.841e-011
       log Kow used: 12.11 (estimated)
       no-melting pt equation used
     Water Sol (Exper. database match) =  0.0001 mg/L (25 deg C)
        Exper. Ref:  HARDY,ML & SMITH,RL (1999); < 0.1 ppb

 Water Sol Estimate from Fragments:
    Wat Sol (v1.01 est) =  2.5606e-006 mg/L

 ECOSAR Class Program (ECOSAR v1.00):
    Class(es) found:       Neutral Organics

 Henrys Law Constant (25 deg C) [HENRYWIN v3.20]:
   Bond Method :   1.19E-008  atm-m3/mole  (1.20E-003 Pa-m3/mole)
   Group Method:   4.45E-008  atm-m3/mole  (4.51E-003 Pa-m3/mole)
 For Henry LC Comparison Purposes:
   User-Entered Henry LC:  not entered
   Henrys LC [via VP/WSol estimate using User-Entered or Estimated values]:
      HLC:  2.075E-001 atm-m3/mole  (2.102E+004 Pa-m3/mole)
      VP:   4.67E-012 mm Hg (source: MPBPVP)
      WS:   2.84E-011 mg/L (source: WSKOWWIN)

 Log Octanol-Air Partition Coefficient (25 deg C) [KOAWIN v1.10]:
  Log Kow used:  12.11  (KowWin est)
  Log Kaw used:  -6.313  (HenryWin est)
      Log Koa (KOAWIN v1.10 estimate):  18.423
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     Log Koa (experimental database):  None

 Probability of Rapid Biodegradation (BIOWIN v4.10):
   Biowin1 (Linear Model)         :  -0.6806
   Biowin2 (Non-Linear Model)     :   0.0000
 Expert Survey Biodegradation Results:
   Biowin3 (Ultimate Survey Model):  -0.3386  (recalcitrant)
   Biowin4 (Primary Survey Model) :   1.0059  (recalcitrant)
 MITI Biodegradation Probability:
   Biowin5 (MITI Linear Model)    :  -0.2784
   Biowin6 (MITI Non-Linear Model):   0.0001
 Anaerobic Biodegradation Probability:
   Biowin7 (Anaerobic Linear Model):  1.0141
 Ready Biodegradability Prediction:   NO

Hydrocarbon Biodegradation (BioHCwin v1.01):
    Structure incompatible with current estimation method!

 Sorption to aerosols (25 Dec C)[AEROWIN v1.00]:
  Vapor pressure (liquid/subcooled):  6.32E-007 Pa (4.74E-009 mm Hg)
  Log Koa (Koawin est  ): 18.423
   Kp (particle/gas partition coef. (m3/ug)):
       Mackay model           :  4.75
       Octanol/air (Koa) model:  6.5E+005
   Fraction sorbed to airborne particulates (phi):
       Junge-Pankow model     :  0.994
       Mackay model           :  0.997
       Octanol/air (Koa) model:  1

 Atmospheric Oxidation (25 deg C) [AopWin v1.92]:
   Hydroxyl Radicals Reaction:
      OVERALL OH Rate Constant =   0.0337 E-12 cm3/molecule-sec
      Half-Life =   317.534 Days (12-hr day; 1.5E6 OH/cm3)
   Ozone Reaction:
      No Ozone Reaction Estimation
   Fraction sorbed to airborne particulates (phi):
      0.996 (Junge-Pankow, Mackay avg)
      1 (Koa method)
    Note: the sorbed fraction may be resistant to atmospheric oxidation

 Soil Adsorption Coefficient (KOCWIN v2.00):
      Koc    :  2.762E+005  L/kg (MCI method)
      Log Koc:  5.441       (MCI method)
      Koc    :  4.78E+007  L/kg (Kow method)
      Log Koc:  7.679       (Kow method)

 Aqueous Base/Acid-Catalyzed Hydrolysis (25 deg C) [HYDROWIN v2.00]:
    Rate constants can NOT be estimated for this structure!

 Bioaccumulation Estimates (BCFBAF v3.00):
   Log BCF from regression-based method = 1.620 (BCF = 41.71 L/kg wet-wt)
   Log Biotransformation Half-life (HL) = 2.7638 days (HL = 580.5 days)
   Log BCF Arnot-Gobas method (upper trophic) = -0.039 (BCF = 0.9147)
   Log BAF Arnot-Gobas method (upper trophic) = 0.841 (BAF = 6.929)
       log Kow used: 12.11 (estimated)

 Volatilization from Water:
```

```
   Henry LC:  4.45E-008 atm-m3/mole  (estimated by Group SAR Method)
   Half-Life from Model River: 4.075E+004  hours   (1698 days)
   Half-Life from Model Lake : 4.448E+005  hours   (1.853E+004 days)

 Removal In Wastewater Treatment:
   Total removal:              94.04  percent
   Total biodegradation:        0.78  percent
   Total sludge adsorption:    93.26  percent
   Total to Air:                0.00  percent
     (using 10000 hr Bio P,A,S)

 Removal In Wastewater Treatment:
   Total removal:              94.04  percent
   Total biodegradation:        0.78  percent
   Total sludge adsorption:    93.26  percent
   Total to Air:                0.00  percent
     (using Biowin/EPA draft method)

 Level III Fugacity Model:
   Mass Amount    Half-Life    Emissions
        (percent)       (hr)       (kg/hr)
  Air       0.114           7.62e+003    1000
  Water     4.26            4.32e+003    1000
  Soil      95.6            8.64e+003    1000
  Sediment  0.00236         3.89e+004    0
    Persistence Time: 7.26e+003 hr
```

ECOSAR Results for Decabromodiphenyl Ether:

```
SMILES : O(c(c(c(c(c1Br)Br)Br)Br)c1Br)c(c(c(c(c2Br)Br)Br)Br)c2Br
CHEM   : Benzene, 1,1 -oxybis[2,3,4,5,6-pentabromo-
CAS Num: 001163-19-5
ChemID1:
ChemID2:
ChemID3:
MOL FOR: C12 Br10 O1
MOL WT : 959.17
Log Kow: 12.11  (KowWin estimate)
Melt Pt:
Wat Sol: 0.0001 mg/L  (experimental database)

ECOSAR v1.00 Class(es) Found
------------------------------
Neutral Organics
                                          Predicted
ECOSAR Class             Organism          Duration  End Pt   mg/L (ppm)
===========================  ==================  ========  ======   ==========
Neutral Organics         : Fish              96-hr     LC50     9.4e-007
Neutral Organics         : Fish              14-day    LC50     1.12e-006
Neutral Organics         : Daphnid             48-hr     LC50    2.36e-006
Neutral Organics         : Green Algae         96-hr     EC50    9.05e-005
Neutral Organics         : Fish              30-day    ChV      1.93e-007
Neutral Organics         : Daphnid                     ChV      1.36e-006
Neutral Organics         : Green Algae                  ChV      0.000187 *
Neutral Organics         : Fish  (SW)          96-hr     LC50    6.06e-007
Neutral Organics         : Mysid Shrimp          96-hr     LC50    6.92e-010
```

```
Neutral Organics          : Fish  (SW)              ChV     4.57e-005
Neutral Organics          : Mysid Shrimp (SW)          ChV     2.99e-012
Neutral Organics          : Earthworm         14-day    LC50      149.184 *

 Note:  * = asterisk designates: Chemical may not be soluble
       enough to measure this predicted effect.

Neutral Organics:
----------------
  For Fish LC50 (96-h), Daphnid LC50, Mysid: If the log Kow is greater
than 5.0, or if the compound is solid and the LC50 exceeds the water
solubility by 10X, no effects at saturation are predicted.

  For Fish LC50 (14-day) and Earthworm LC50: If the log Kow is greater
than 6.0, or if the compound is solid and the LC50 exceeds the water
solubility by 10X, no effects at saturation are predicted.

  For Green Algae Acute Toxicity Values: If the log Kow of the chemical is
greater than 6.4, or if the compound is solid and the EC50 exceeds the water
solubility by 10X, no effects at saturation are predicted for these endpoints.

  For All Chronic Toxicity Values: If the log Kow of the chemical is greater
than 8.0, or if the compound is solid and the ChV exceeds the water solubility
by 10X, no effects at saturation are predicted for these endpoints.

ECOSAR v1.00 SAR Limitations:
----------------------------
Maximum LogKow: 5.0 (Fish 96-hr LC50; Daphnid LC50, Mysid LC50)
Maximum LogKow: 6.0 (Fish 14-day LC50; Earthworm LC50)
Maximum LogKow: 6.4 (Green Algae EC50)
Maximum LogKow: 8.0 (ChV)
Maximum Mol Wt: 1000

-----------------------------------------------------------------------------
```

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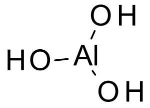
APPENDIX IX C: GREEN SCREEN FOR ALUMINUM TRIHYDROXIDE (CAS #21645-51-2)[5]

Also Called: Aluminum oxide trihydrate, Aluminum trihydroxide, Alumina trihydrate, Aluminic acid

Chemical Structure of Aluminum Trihydroxide:



For Inorganic Chemicals:
Define Form & Physiochemical Properties (Leisewitz 2001)
1. Particle size: 0.1-0.6 µm
2. Structure: Crystalline
3. Mobility: Insoluble in water; soluble in alkaline solutions, acid solutions

Identify Applications/Functional Uses: Flame retardant

Green Screen Rating[6]: Aluminum trihydroxide was assigned a Green Screen Benchmark Score of 2 based on very High persistence (P), Moderate neurotoxicity (N), Moderate systemic toxicity (ST), and Moderate corrosion/irritation (Cr) (2c).

Green Screen (Version 1) Levels of Concern for Aluminum Trihydroxide														
Human – Tier 1					**Human – Tier 2**				**Eco**		**Fate**		**Physical**	
C	**M**	**R/D**	**ED**	**N**	**AT**	**Cr**	**Sn**	**ST**	**AA**	**CA**	**P**	**B**	**Ex**	**F**
L	*L*	**L**	nd	**M**	**L**	**M**	**L**	**M**	**L**	*M*	**vH**	**L**	**L**	**L**

*Endpoints in italics were assigned using estimated values and professional judgment (Structure Activity Relationships).

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[5] CPA recommends independent third-party validation of all Green Screen assessments. No independent third-party validation has been done for this assessment . Companies may not make marketing claims based on a Green Screen assessment that has not undergone an independent validation.

[6] For inorganic chemicals with low human and ecotoxicity across all hazard endpoints and low bioaccumulation, persistence alone will not be deemed problematic. Inorganic chemicals that are only persistent will be evaluated under the criteria for Benchmark 4.

Transformation Products and Ratings:

Identify relevant fate and transformation products (i.e., dissociation products, transformation products, valence states) and/or moieties of concern[7]

Life Cycle Stage	Transformation Pathway	Transformation Products	CAS #	Green Screen Rating
End of life	Dissociation	Al^{3+}	7429-90-5	Present on the Red List of chemicals (CPA 2009).
End of life	Dissociation	OH-	3352-57-6	Not present on the Red List of chemicals (CPA 2009).

*The above transformation products were screened against the CPA's table of Red List chemicals.

Introduction

Aluminum trihydroxide is an additive mineral flame retardant, filler, and an additive for fume reduction (Leisewitz 2001). Because it is a relatively weak-acting flame retardant, it must be utilized in large quantities, which limits its application area. In addition, aluminum trihydroxide decomposes at 200˚C which further limits its application and cannot be used in plastics with high processing temperatures.

Aluminum trihydroxide is primarily used in the manufacturing of glass, ceramics, activated alumina, flame retardants and mattress bedding. It is also used as a rubber reinforcing agent, paper coating, filler, and in cosmetics. Aluminum trihydroxide is also used as an antacid and an antihyperphosphatemic (Lewis 1997).

Human Health – Tier 1

Carcinogenicity (C) Score (H, M or L): L

Aluminum trihydroxide was assigned a score of Low for carcinogenicity based on results from animal studies.

- Not classifiable as a human carcinogen (ACGIH 2008).
- Aluminum hydroxide was not carcinogenic after daily intraperitoneal administration to mice for 4 months at dosages up to 200 mg/kg/day (FAO/WHO 1989).

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[7] A moiety is a discrete chemical entity that is a constituent part or component of a substance. A moiety of concern is often the parent substance itself for organic compounds. For inorganic compounds, the moiety of concern is typically a dissociated component of the substance or a transformation product.

- In a 6 month study in rats the effects of aluminum on renal function were and phosphate handling were studied. Rats (number/strain not reported) were given aluminum hydroxide (80 mg/kg, IP) 3 times/wk. No changes were observed in renal function and no evidence of carcinogenicity was found (Mahieu 1998).

Mutagenicity (M) and Genotoxicity Score (H, M or L): *L*
No mutagenicity and genotoxicity data were identified for aluminum hydroxide. A score of Low was assigned based on the U.S. EPA's assessment on flame retardants in printed circuit boards for aluminum hydroxide (U.S. EPA 2008).

- No relevant data on mutagenicity was identified for aluminum hydroxide.
- Aluminum hydroxide is estimated to be of low genotoxic potential (U.S. EPA 2008).

Reproductive (R) and Developmental (D) Toxicity Score (H, M or L): L
Aluminum trihydroxide was assigned a score of Low for reproductive and developmental toxicity based on negative results from animal studies.

- When high doses (≤ 1094 mg/kg/day) of aluminum hydroxide were orally administered to pregnant rats and mice during embryogenesis, no maternal or developmental toxicity occurred (Bingham 2001).
- No developmental effects occurred in Swiss mice (number not reported) at doses of 66.5, 133, or 266 mg/kg/day following gavage administration on gestation days 6-15 (Domingo 1989).
- No developmental toxicity occurred in Swiss albino CD-1 mice (number not reported) at a dose of 57.5 mg/kg/day following gavage administration on gestation days 6-15 (Colomina 1992).
- No developmental toxicity occurred in Sprague-Dawley rats (number not reported) at a gavage dose of 384 mg/kg/day on gestation days 6-15 (Gomez 1991).
- No developmental toxicity occurred in Wistar rats (number not reported) at gavage doses of 192, 384, and 768 mg/kg/day (Gomez 1990).

Endocrine Disruption (ED) Score (H, M or L): nd

- Aluminum trihydroxide is not listed as a potential endocrine disruptor on the EU Priority List of Suspected Endocrine Disruptors.
- Aluminum trihydroxide is not listed as a potential endocrine disruptor on the OSPAR List of Chemicals of Possible Concern.
- Aluminum trihydroxide is not listed as a potential endocrine disruptor on the Red List of Chemicals (CPA 2009).

Neurotoxicity (N) Score (H, M or L): M
Aluminum trihydroxide was assigned a score of Moderate for neurotoxicity based on results from animal studies and being present on the red list as a potential neurotoxicant.

- In a 30-day study rats (number/strain not reported) were fed aluminum in an oral diet with no significant effects noted and a reported NOAEL of 1252 mg/kg/day (ASTDR 2008).

- In a 90-day study rats (number/strain not reported) were given aluminum hydroxide with citric acid by oral gavage and demonstrated impaired learning in a labyrinth maze test. A LOAEL of 35 mg/kg/day was reported (ASTDR 2008).
- Aluminum hydroxide is expected to be of moderate hazard for neurotoxicity based on available data (U.S. EPA 2008).

Human Health – Tier 2

Acute Mammalian (AT) Toxicity Score (H, M or L): L

A score of Low for acute mammalian toxicity was assigned to aluminum trihydroxide based on an oral LD_{50} value greater than 5,000 mg/kg-bw. Data is from one route of exposure in two different species.

- *Oral*: TDL_0 (child) = 79,000 mg/kg (ChemIDplus 2010)
- *Oral*: TDL_0 (child) = 122,000 mg/kg (ChemIDplus 2010)
- *Oral*: LD_{50} (rat) > 5,000 mg/kg (ESIS 2000)

Corrosion/ Irritation (Skin/ Eye) (Cr) Score (H, M or L): M

Aluminum trihydroxide was assigned a score of Moderate for corrosion and irritation based on human studies and MSDS data.

- Aluminum trihydroxide may cause mild skin, eye and upper respiratory tract irritation (ScienceLab 2010).

Sensitization (Sn) Score (Skin and Respiratory) (H, M or L): L

Aluminum trihydroxide was assigned a score of Low for sensitization based on aluminum hydroxide testing negative for skin and respiratory sensitization.

- *Dermal*: Aluminum trihydroxide was not sensitizing. No other details were provided (ESIS 2000).
- *Respiratory/Dermal:* Aluminum trihydroxide was not sensitizing. No other details were provided (ESIS 2000).

Systemic/ Organ (ST) Toxicity Score (includes organ effects and immunotoxicity) (H, M or L): M

Aluminum trihydroxide was assigned a score of Moderate for systemic/organ toxicity based on potential immunotoxic effects in humans.

- The effects of dietary administration of aluminum hydroxide were examined in male Sprague-Dawley rats. Groups of 25 rats were fed a diet containing 14,470 ppm aluminum hydroxide or a control diet for 28 days. The mean daily aluminum dose was calculated as 302 mg/kg body weight/day. Dietary administration of aluminum hydroxide did not induce any signs of toxicity. Clinical observations during the 28-day treatment period and the recovery phase were similar in control and treated rats. There were no significant changes in hematology, clinical chemistry parameters, or organ weights (Hicks 1987).

- In a 6-week oral administration study in humans, a reduction in primed cytotoxic T-cells was observed and a LOAEL of 25 mg/kg/day was reported (ATSDR 2008).

Ecotoxicity

Acute Aquatic (AA) Toxicity Score (H, M or L): L

Aluminum trihydroxide was assigned a score of Low for acute aquatic toxicity based on LC_{50} values greater than 100 mg/L.

- 96-hour LC_{50} (*fish*) > 100 mg/L (ESIS 2000)
- 48-hour LC_{50} (*Daphnia magna*) > 100 mg/L (ESIS 2000)
- 72-hour EC_{50} (*Selenastrum capricornutum*) > 100 mg/L (ESIS 2000)

Chronic Aquatic (CA) Toxicity Score (H, M or L): *M*

No data was identified for aluminum trihydroxide. Aluminum trihydroxide was assigned a score of Moderate chronic aquatic toxicity based GHS criteria for chronic aquatic toxicity.

- There were no data identified on the chronic aquatic toxicity of aluminum hydroxide. The globally harmonized system (GHS) Categorization of poorly soluble substances for which no chronic or acute toxicity data exist are classified as chronic aquatic toxicity category 4, a ―safety net” category. The Green Screen assigns these chemicals a rating of ―moderate.”

Environmental Fate

Persistence (P) Score (vH, H, M, or L): vH

Aluminum trihydroxide was assigned a score of very High for persistence based on the chemical being an inorganic compound and not having any identifiable biodegradation pathways at normal environmental conditions.

- As an oxidized inorganic compound, aluminum trihydroxide is not expected to biodegrade, oxidize further in air, or undergo hydrolysis at environmental conditions. No degradation process for aluminum trihydroxide could be identified at typical environmental conditions (US EPA 2008).

Bioaccumulation (B) Score (vH, H, M, or L): L

Aluminum trihydroxide was assigned a score of Low for bioaccumulation based on a BCF value less than 100.

- Aluminum hydroxide has a predicted BCF of 3.2 (U.S. EPA 2008).
- Aluminum hydroxide is not expected to be bioaccumulative (U.S. EPA 2008).

Physical Properties

Explosivity (Ex) Hazard Rating (H, M or L): L

Aluminum trihydroxide was assigned a Low for explosivity because no basis for concern was identified.

- Aluminum hydroxide is not explosive (ESIS 2000)

Flammability (F) Hazard Rating (H, M or L): L

Aluminum trihydroxide was assigned a Low for flammability because no basis for concern was identified.

- Aluminum hydroxide is not flammable (ESIS 2000)

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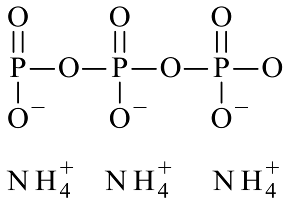
APPENDIX IX D: GREEN SCREEN FOR AMMONIUM POLYPHOSPHATE (CAS #68333-79-9)[8]

Also Called: AP 422, AP 462, APP (fireproofing agent), APP 422, Albaplas AP 95, Aluminum polyphosphate, Amgard CL, Amgard MC, Amgard TR, Ammonium ortho and polyphosphate solution, Ammonium orthophosphate, superphosphate, Ammonium polyphosphate, Ammonium polyphosphates, Antiblaze MC, Antiblaze MCM, Budit 3076, Budit 3076DC, Budit 3077, Budit 365, DFP-I, EINECS 269-789-9, EXO 462, Exolit 263, Exolit 422, Exolit 442, Exolit 454, Exolit 455, Exolit 462, Exolit 470, Exolit AP 422, Exolit AP 423, Exolit AP 462, FR-Cros 480, FR-Cros 484,Fire-Trol LCG-R, Flameguard PT 8, Hostaflam 423, Hostaflam AP 420, Hostaflam AP 422, Hostaflam AP 462, Hostaflam AP 464, Hostaflam TP-AP 751, Hostaflam TP-AP 752, Novawhite, Phos-Chek P 30, Phos-Chek P 40, Phos-Chek P 60, Poly-N 10-34-0, Poly-N 11-37-0, Polymetaphosphoric acid, ammonium salt, Polyphosphoric acid, ammonium salt, Sumisafe, Taien A, Taien H

Chemical Structure of Ammonium Polyphosphate:



$$\begin{array}{ccccc} O & & O & & O \\ \| & & \| & & \| \\ P & -O- & P & -O- & P-O \\ | & & | & & | \\ O^- & & O^- & & O^- \\ & & & & \\ NH_4^+ & & NH_4^+ & & NH_4^+ \end{array}$$

***Note:** Data gaps for ammonium polyphosphate (CAS #6833-79-9) were addressed using the structurally similar chemical sodium tripolyphosphate (CAS #7758-29-4). The National Academy of Sciences selected sodium tripolyphosphate as a chemical surrogate for ammonium polyphosphate in the report ―Toxicological Risks of Selected Flame-Retardant Chemicals (NAS 2000)."

For Polymers: Identify Monomers and Corresponding Properties

1. % of Each Monomer – n/a
2. Are the monomers blocked? – n/a
3. Molecular Weight (MW) of Polymer – ca 100,000 g/mol (Pinfa 2010).
4. % of Polymer with
   a) MW <500 – n/a
   b) MW <1,000 – n/a
5. % Weight Residual Monomers – n/a
6. Solubility/Dispersability/Swellability – ≤ 5 g/L (Clariant 2009)
7. Particle Size – approx. 15 µm (Clariant 1999)
8. Overall Polymer Charge – n/a

---

[8] CPA recommends independent third-party validation of all Green Screen assessments. No independent third-party validation has been done for this assessment . Companies may not make marketing claims based on a Green Screen assessment that has not undergone an independent validation.

Identify Applications/Functional Uses: Flame retardant

Green Screen Rating[9]: Ammonium polyphosphate was assigned a Green Screen Benchmark Score of 4 based on low human toxicity and ecotoxicity.

Green Screen (Version 1) Levels of Concern for Ammonium Polyphosphate														
Human – Tier 1					Human – Tier 2				Eco		Fate		Physical	
C	M	R/D	ED	N	AT	Cr	Sn	ST	AA	CA	P	B	Ex	F
L	L	*L*	nd	nd	L	L	L	*L*	L	*L*	L	L	L	L

*Endpoints in italics were assigned using estimated values and professional judgment (Structure Activity Relationships)

Transformation Products and Ratings:

Identify relevant fate and transformation products (i.e., dissociation products, transformation products, valence states) and/or moieties of concern[10]

Life Cycle Stage	Transformation Pathway	Transformation Products	CAS #	Green Screen Rating
End of Life	Water hydrolysis	Ammonium phosphate	7783-28-0 (USAN) and 10124-31-9	Not present on the Red List of chemicals (CPA 2009).
End of Life	Combustion	Ammonia	7664-41-7	Not present on the Red List of chemicals (CPA 2009).
End of Life	Combustion	Phosphorous oxides	1314-56-3 and 14452-66-5	Not present on the Red List of chemicals (CPA 2009).
End of Life	Combustion	Nitrogen oxides	10102-43-9	Not present on the Red List of chemicals (CPA 2009).

*The above transformation products were screened against the CPA's table of Red List chemicals; none were found.

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[9] For inorganic chemicals with low human and ecotoxicity across all hazard endpoints and low bioaccumulation, persistence alone will not be deemed problematic. Inorganic chemicals that are only persistent will be evaluated under the criteria for Benchmark 4.

[10] A moiety is a discrete chemical entity that is a constituent part or component of a substance. A moiety of concern is often the parent substance itself for organic compounds. For inorganic compounds, the moiety of concern is typically a dissociated component of the substance or a transformation product.

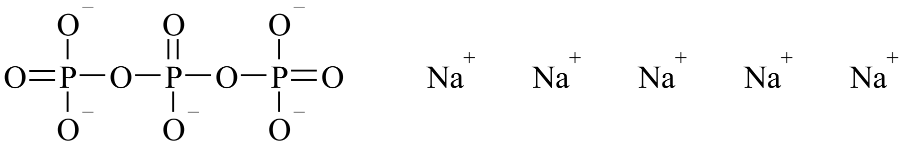
Introduction

Ammonium polyphosphate (―APP”) is a solid, ionic, non-volatile polymer used for flame retardation (Clariant 2009). This white powder has a molecular weight of ca 100,000 g/mol and is almost completely insoluble in water and is completely insoluble in organic solvents (Pinfa 2010). The log K_{ow} is not applicable to APP because it is an inorganic salt and therefore will not partition between organic and aqueous phases (UNEP 2008). No PEL, STEL or TLV have been established for APP.

APP is an intumescent coating, meaning it swells as a result of heat exposure and produces a carbonaceous foam which is poor conductor of heat, thus retarding heat transfer (Clariant 1999). APP has excellent flame retardant characteristics in cellulose-containing materials such as paper and wood products but is also classified for use on steel and plastic surfaces as well as adhesives and sealants (Clariant 1999). APP is also used as a fertilizer (UNEP 2008).

Because there no relevant toxicity data were identified for the possible reproductive, developmental, acute and systemic toxicity of APP, a structurally similar surrogate was used. Sodium tripolyphosphate was selected as the chemical surrogate due to its structural similarity, use as a flame retardant, and use as a surrogate in several previous reports (NAS 2000).

Chemical Structure of Chemical Surrogate:



$$O{=}\overset{O^-}{\underset{O^-}{P}}{-}O{-}\overset{O}{\underset{O^-}{\overset{\|}{P}}}{-}O{-}\overset{O^-}{\underset{O^-}{P}}{=}O \quad Na^+ \quad Na^+ \quad Na^+ \quad Na^+ \quad Na^+$$

Sodium Tripolyphosphate (CAS #7758-29-4)

Human Health – Tier 1

Carcinogenicity (C) Score (H, M or L): L

APP was assigned a score of Low for carcinogenicity because no basis for concern was identified.

- APP is not listed as a known carcinogen by IARC, NTP, U.S. EPA, or CA Prop 65.

Mutagenicity (M) and Genotoxicity Score (H, M or L): L

APP was assigned a score of Low for mutagenicity and genotoxicity based on negative test results from several Ames assays.

- APP tested negative for mutagenicity in an Ames Test. No additional information provided (Pinfa 2010).
- In separate assays, APP (Exolit 422, technical quality) and Exolit 456 (90% APP and 10% melamine/formaldehyde) tested negative for mutagenicity in *Salmonella*

typhimurium tester strains TA 98, TA 100, TA 1535, TA 1537, and TA 1538, and *Escherichia coli* WP2uvrA with and without a metabolic activator at concentrations ranging from 4 to 5000 µg/plate in either a water or a DMSO vehicle (ESIS 2000).

Reproductive (R) and Developmental (D) Toxicity Score (H, M or L): *L*
Because no reproductive or developmental toxicity data were identified for APP, the structurally similar sodium tripolyphosphate was used as a surrogate. APP was assigned a score of Low based on analog data for sodium tripolyphosphate, which had no adverse effects on reproductive or developmental health.

Sodium tripolyphosphate

- Sodium tripolyphosphate had no effect on fertility, litter size, neonate growth, or neonate survival in a three generation reproduction study in rats administered 500 mg/kg-bw/day[11] sodium tripolyphosphate in their feed. No other details for this study were provided (NAS 2000).

Endocrine Disruption (ED) Score (H, M or L): nd

- APP is not listed as a potential endocrine disruptor on the EU Priority List of Suspected Endocrine Disruptors.
- APP is not listed as a potential endocrine disruptor on the OSPAR List of Chemicals of Possible Concern.
- APP is not listed as a potential endocrine disruptor on the Red List of Chemicals (CPA 2009).

Neurotoxicity (N) Score (H, M or L): nd

- APP is not classified as a developmental neurotoxicant (Grandjean and Landrigan 2006).
- APP is not listed as a potential neurotoxicant on the Red List of Chemicals (CPA 2009).

Human Health – Tier 2

Acute Mammalian (AT) Toxicity Score (H, M or L): L
APP was assigned a score of Low for acute mammalian toxicity based on oral and dermal LD_{50} values greater than 2,000 mg/kg-bw. Data was from three different routes in two different species.

- *Oral*: An LD_{50} of > 2,000 mg/kg-bw was identified in the rat (UNEP 2008).
- *Oral*: An LD_{50} of 4,740 mg/kg-bw was identified in the rat (Clariant 2009).
- *Oral*: An LD_{50} of > 2,000 mg/kg-bw was identified in the rabbit (UNEP 2008).
- *Inhalation*: An LC_{50} of > 5.09 mg/L (4-hr exposure) was identified in the rat (UNEP 2008).

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[11] The original report by Hodge (1964a) provides a concentration of 0.5% sodium tripolyphosphate administered to rats. The conversion to mg/kg-bw/day is as follows (assuming use of Fisher rat, as the strain is not provided in the study):
(5,000 mg sodium tripolyphosphate/kg chow * 0.018 kg chow/day)/0.180 kg-bw = 500 mg/kg-bw/day

- *Dermal*: An LD_{50} of >5,000 mg/kg-bw was identified in the rat (UNEP 2008).
- *Dermal*: An LD_{50} of >2,000 mg/kg-bw was identified in the rat (UNEP 2008).

Corrosion/ Irritation (Skin/ Eye) (Cr) Score (H, M or L): L

APP was assigned a score of Low for corrosion and irritation based on animal studies that showed the chemical to not be irritating to the skin or eyes of rabbits.

- *Dermal*: APP was not irritating to the skin of rabbits following a 4-hour occlusion in a Draize test. The test substance was 70% ammonium polyphosphate and 30% monoammonium phosphate. Additional details concerning this study were not provided (UNEP 2008).
- *Dermal*: APP was slightly irritating to the skin of rabbits following a 24-hour occlusive Patch test. Additional details concerning this study were not provided (ESIS 2000).
- *Dermal*: Exolit 456 (90% APP and 10% monoammonium phosphate) was not irritating in an OECD 404 ―Acute Dermal irritation/corrosion" test. Additional details concerning this study were not provided (ESIS 2000).
- *Ocular*: APP was not irritating to the eyes of rabbits in a Draize test. The test substance was 70% ammonium polyphosphate and 30% monoammonium phosphate. Additional details concerning this study were not provided (ESIS 2000).
- *Ocular*: APP was not irritating to the eyes of rabbits. Additional details concerning this study were not provided (ESIS 2000).
- Ocular: Exolit 456 (90% APP and 10% melamine/formaldehyde) was not irritating to the eyes of rabbits following an OECD 405 ―Acute Eye Irritation/Corrosion" test. Additional details concerning this study were not available (ESIS 2000).

Sensitization (Sn) Score (Skin and Respiratory) (H, M or L): L

APP was assigned a score of Low for sensitization because animal tests showed the chemical to be a poor sensitizing agent.

- *Dermal*: APP was found to be a poor skin-sensitizing agent in the Magnusson and Kligman maximization test. Twenty female guinea pigs were initially injected intradermally with a 25% (w/v) solution of APP. Topical induction was then attempted on day 7 with filter paper patches containing 75% (w/w) APP in distilled water. Only 1 of 20 animals had skin changes (scattered mild redness) at the application site 1 hour after removal of the patches. No animals had any visible skin reactions 24 hours after patch removal. None of the animals showed any tissue reaction either 24 or 48 hours after topical challenge with filter paper patches containing 50% or 75% solutions of APP. No other data was provided for this study (Safepharm 1993).

Systemic/ Organ (ST) Toxicity Score (includes organ effects and immunotoxicity) (H, M or L): *L*

Because no relevant systemic/organ toxicity data were identified for APP, the structurally similar sodium tripolyphosphate was used as a surrogate. APP was assigned a score of Low for systemic/organ toxicity based on analog data.

Sodium tripolyphosphate:

- Male and female rats (36/sex/dose) were administered 0, 3, and 5% sodium tripolyphosphate in their diets for 24 weeks. Nephrocalcinosis was observed at 3% dose level only. No other information was provided (JECFA 1974).

Ecotoxicity

Acute Aquatic (AA) Toxicity Score (H, M or L): L

APP was assigned a score of Low for acute aquatic toxicity based on LC_{50} values of 100 mg/L or greater.

- APP has an LC_{50} of > 101 mg/L in *Oncorhynchus mykiss* (freshwater fish, 96 hour) (UNEP 2008).
- APP has an LC_{50} of 100 - 1,000 mg/L in *Danio rerio* (freshwater fish, 96 hour) (Clariant 2009).

Chronic Aquatic (CA) Toxicity Score (H, M or L): *L*

APP was assigned a Low for chronic aquatic toxicity based on professional opinion.

- APP has a molecular weight of 100,000 g/mol (Pinfa 2010). Insoluble polymers are not expected to be toxic to aquatic organisms unless the material is in the form of finely divided particles. Toxicity of these polymer particles does not depend on a specific structural feature, but occurs from occlusion of respiratory organs such as gills. For these polymers, toxicity occurs at high concentrations; >100 mg/L for acute toxicity and >10 mg/L for chronic toxicity (U.S. EPA 2010).

Environmental Fate

Persistence (P) Score (vH, H, M, or L): L

APP was assigned a score of Low for persistence based on a soil half-life less than 30 days and rapid biodegradation.

- APP breaks down into ammonia and phosphate rapidly in soil and sewage sludge (Leisewitz 2000).
- Hydrolysis of APP occurs very slowly in neutral solutions (UNEP 2008).
- The half-life of APP in soil ranged from 1.6 to 2.0 days under anaerobic conditions and from 5.3 to 8.7 days under aerobic conditions (UNEP 2008).
- Biodegradation tests are not applicable to APP because the methods are based on carbon oxidation and the ammonium present in APP may be nitrified (UNEP 2008).

Bioaccumulation (B) Score (vH, H, M, or L): L

APP was assigned a score of Low for bioaccumulation based on its insolubility.

- APP is not expected to bioaccumulate because it is an inorganic polymer (avg. MW = 100,000) and therefore insoluble in water (Pinfa 2010).

Physical Properties

Explosivity (Ex) Hazard Rating (H, M or L): L

APP was assigned a score of Low for explosivity because no basis for concern was identified.

- APP is not explosive- no other data provided (Clariant 2009).

Flammability (F) Hazard Rating (H, M or L): L

APP was assigned a score of Low for flammability because no basis for concern was identified.

- APP is not flammable- no other data provided (Clariant 2009).

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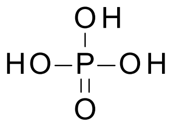
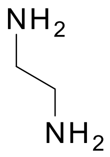
APPENDIX IX E: GREEN SCREEN FOR ETHYLENEDIAMINE PHOSPHATE (CAS #14582-17-6)[12]

Also Called: 1,2-Ethanediamine, phosphate, Ethylenediamine, salt with phosphoric acid

Chemical Structure of Ethylenediamine Phosphate:



$\mathrm{HO{-}P(OH)({=}O){-}OH}$



***Note:** Data gaps for ethylene phosphate (CAS #14852-17-6) were addressed using the individual components of this mixture, ethylenediamine (CAS #107-15-3) and phosphoric acid (CAS #7664-38-2) as chemical surrogates.

For Inorganic Chemicals:
Define Form & Physiochemical Properties

4. Particle size (e.g. silica of respirable size) – n/a
5. Structure (e.g. amorphous vs. crystalline) – n/a
6. Mobility (e.g. Water solubility, volatility) – n/a

Identify Applications/Functional Uses: Flame retardant

Green Screen Rating[13]: Ethylenediamine phosphate was assigned a Green Screen Benchmark Score of 2 based on High chronic aquatic toxicity (CA), Moderate mutagenicity (M) and reproductive and developmental toxicity (R/D) (2d).

Green Screen (Version 1.0) Levels of Concern for Ethylenediamine Phosphate														
Human – Tier 1					**Human – Tier 2**				**Eco**		**Fate**		**Physical**	
C	**M**	**R/D**	**ED**	**N**	**AT**	**Cr**	**Sn**	**ST**	**AA**	**CA**	**P**	**B**	**Ex**	**F**
L	*M*	*M*	nd	nd	*M*	*H*	*H*	*M*	**L**	**H**	**M**	**L**	**L**	**L**

*Endpoints in italics were assigned using estimated values and professional judgment (Structure Activity Relationships).

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[12] CPA recommends independent third-party validation of all Green Screen assessments. No independent third-party validation has been done for this assessment . Companies may not make marketing claims based on a Green Screen assessment that has not undergone an independent validation.

[13] For inorganic chemicals with low human and ecotoxicity across all hazard endpoints and low bioaccumulation, persistence alone will not be deemed problematic. Inorganic chemicals that are only persistent will be evaluated under the criteria for Benchmark 4.

Transformation Products and Ratings:
Identify relevant fate and transformation products (i.e., dissociation products, transformation products, valence states) **and/or moieties of concern**[14]

Life Cycle Stage	Transformation Pathway	Transformation Products	CAS #	Green Screen Rating
End of life	Dissociation	Ethylenediamine	107-15-3	Present on the Red List of chemicals (CPA 2009).
End of life	Dissociation	Phosphoric acid	7664-38-2	Not present on the Red List of chemicals (CPA 2009).
End of life	Combustion	Carbon oxides	630-08-0 and 124-38-9	Present on the Red List of chemicals (CPA 2009).
End of Life	Combustion	Phosphorous oxides	1314-56-3 and 14452-66-5	Not present on the Red List of chemicals (CPA 2009).
End of Life	Combustion	Nitrogen oxides	10102-43-9	Not present on the Red List of chemicals (CPA 2009).

*The above transformation products were screened against the CPA‘s table of Red List chemicals.

Introduction

Ethylenediamine phosphate (CAS #14852-17-6) is a non-halogenated flame retardant composed of a mixture of ethylenediamine and phosphoric acid. No PEL, STEL or TLV have been established for ethylenediamine phosphate. Because there no relevant toxicity data were identified to assess possible skin/eye corrosion, skin/respiratory sensitization, mutagenicity, reproductive, developmental, acute or systemic toxicity of ethylenediamine phosphate, individual components of EDP were evaluated to address datagaps: ethylenediamine (CAS #107-15-3) and phosphoric acid (CAS #7664-38-2).

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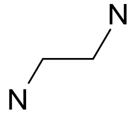
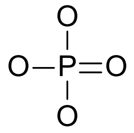
[14] A moiety is a discrete chemical entity that is a constituent part or component of a substance. A moiety of concern is often the parent substance itself for organic compounds. For inorganic compounds, the moiety of concern is typically a dissociated component of the substance or a transformation product.

Chemical Structure of Surrogates:



Ethylenediamine (CAS #107-15-3)



Phosphoric acid (CAS #7664-38-2)

Human Health – Tier 1

Carcinogenicity (C) Score (H, M or L): L
Ethylenediamine phosphate was assigned a score of Low for carcinogenicity because no basis for concern was identified.

- Ethylenediamine phosphate is not listed as a known carcinogen by IARC, NTP, U.S. EPA, or CA Prop 65.

Mutagenicity (M) and Genotoxicity Score (H, M or L): *M*
Because no mutagenicity and genotoxicity data were identified for ethylenediamine phosphate, the components of the mixture were used as a surrogate. Ethylenediamine phosphate was assigned a score of Moderate for mutagenicity and genotoxicity based on conflicting results from several genotoxicity studies.

<u>Ethylenediamine</u>

- *In vitro* - An Ames Reverse Mutation assay was performed using *Salmonella typhimurium* tester strains TA100 and TA1535 in the presence and absence of metabolic activation at concentrations ranging from 0-6667 µg/plate and determined to be positive for mutagenicity (UNEP 2001).
- *In vitro* - An Ames Reverse Mutation assay was performed using *Salmonella typhimurium* tester strains TA98 and TA1537 in the presence and absence of metabolic activation at concentrations ranging from 0-3333 µg/plate and determined to be negative for mutagenicity (UNEP 2001).
- *In vitro* - An Ames Reverse Mutation assay was performed using *Salmonella typhimurium* tester strains TA98, TA100, TA 1535, TA 1537 and TA1538 in the presence and absence of metabolic activation at concentrations ranging from 90-9000 µg/plate and determined to be negative for mutagenicity (UNEP 2001).
- *In vitro* - An Ames Reverse Mutation assay was performed using *Salmonella typhimurium* tester strains TA98, TA100, TA 1535, and TA 1537 in the presence and absence of metabolic activation at concentrations ranging from 0-5000 µg/plate. Mutagenicity was ambiguous in TA 100 with metabolic activation, and negative in all other strains (UNEP 2001).
- *In vitro* – An HGPRT assay was performed using Chinese hamster ovary cells in the presence and absence of metabolic activation at concentrations ranging from 0-897 µg/plate and found to be negative for mutagenicity (UNEP 2001).
- *In vitro* – A sister chromatid exchange assay was performed using Chinese hamster ovary cells in the presence and absence of metabolic activation at concentrations ranging from 0-448 µg/plate and found to be negative for mutagenicity (UNEP 2001).

Phosphoric acid

- *In vitro* - An Ames Reverse Mutation assay was performed using *Salmonella typhimurium* tester strains TA97, TA98, TA100, and TA104 in the presence and absence of metabolic activation at concentrations ranging from 917-3668 µg/plate and determined to be negative for mutagenicity (CCRIS 2010).
- *In vitro* - An Ames Reverse Mutation assay was performed using *Salmonella typhimurium* tester strains in the presence and absence of metabolic activation and determined to be negative for mutagenicity. Strains and concentrations were not reported (ESIS 2000).

Reproductive (R) and Developmental (D) Toxicity Score (H, M or L): *M*
Because no reproductive and developmental toxicity data were identified for ethylenediamine phosphate, the components of the mixture were used as a surrogate. Ethylenediamine phosphate was assigned a score of Moderate for reproductive and developmental toxicity based on animal studies for ethylenediamine.

Ethylenediamine

- A 2-generation reproductive study was conducted on F344 rats (13 male and 26 female/dose level). Ethylenediamine was administered at concentrations of 50, 150, and 500 mg/kg by oral feeding daily starting 100 days prior to mating of F_0 until weaning of F_2 rats. Significant reduction in parental body weight gain was observed in the 150 and 500 mg/kg groups of male and female rats. A higher incidence of hepatocellular pleomorphism in both sexes of the 500 mg/kg group was observed and a significant decrease in the prevalence of kidney tubular mineralization in female rats at 150 mg/kg. No evidence of fertility impairment or embryotoxic effects was observed. A parental NOAEL of 50 mg/kg and a F_1 offspring NOAEL of 150 mg/kg were reported by the authors (UNEP 2001).
- A development toxicity study was performed on New Zealand White rabbits (26/dose). Rabbits were administered 0, 10, 40, and 80 mg/kg of ethylenediamine (purity not reported) on gestation days six through nineteen. No significant effects were observed on maternal food intake, body weight gain, liver or kidney weight, or uterine weight. No effects were observed on viability, litter size, fetal weight or fetal morphology. A NOAEL of > 80 mg/kg for maternal and fetal toxicity was reported by the authors (UNEP 2001).

Phosphoric acid

- A 1-generation reproductive study was conducted on rats (strain/sex/number not reported). Phosphoric acid was administered at concentrations of 180 and 375 mg/kg by oral feeding for 29 weeks. No harmful effects on the growth of the offspring or parental rats were reported at the highest concentration (ESIS 2000).

Endocrine Disruption (ED) Score (H, M or L): nd

- Ethylenediamine phosphate is not listed as a potential endocrine disruptor on the EU Priority List of Suspected Endocrine Disruptors.
- Ethylenediamine phosphate is not listed as a potential endocrine disruptor on the OSPAR List of Chemicals of Possible Concern.
- Ethylenediamine phosphate is not listed as a potential endocrine disruptor on the Red List of Chemicals (CPA 2009).

Neurotoxicity (N) Score (H, M or L): nd

- Ethylenediamine phosphate is not classified as a developmental neurotoxicant (Grandjean and Landrigan 2006).
- Ethylenediamine phosphate is not listed as a potential neurotoxicant on the Red List of Chemicals (CPA 2009).

Human Health – Tier 2

Acute Mammalian (AT) Toxicity Score (H, M or L): *M*

Because no acute mammalian toxicity data were identified for ethylenediamine phosphate, the components of the mixture were used as a surrogate. A score of Moderate for acute mammalian toxicity was assigned to ehtylenediamine phosphate based on oral LD_{50} values between 50 and 2,000 mg/kg-bw and dermal LD_{50} values between 200 and 2,000 mg/kg-bw. Data is from two surrogates using three different routes in three different species.

Ethylenediamine

- *Oral*: LD_{50} (rat) = 637 mg/kg (UNEP 2001).
- *Oral*: LD_{50} (rat) = 1850 mg/kg (UNEP 2001).
- *Oral*: LD_{50} (rat) = 1050 mg/kg (UNEP 2001).
- *Oral*: LD_{50} (rat) = 1500 mg/kg (UNEP 2001).
- *Oral*: LD_{50} (mouse) = 1000 mg/kg (ChemIDPlus 2010).
- *Dermal*: LD_{50} (rabbit) = 560 mg/kg (UNEP 2001).
- *Dermal*: LD_{50} (rat) = 1000 mg/kg (UNEP 2001).
- *Inhalation*: LC_{50} (rat) = 29 mg/L (ChemIDPlus 2010).

Phosphoric acid

- *Oral*: LD_{50} (rat) = 1530 mg/kg (ESIS 2000).
- *Dermal*: LD_{50} (rabbit) = 2740 mg/kg (ESIS 2000).
- *Inhalation*: LC_{50} (rabbit) = 1.689 mg/L (ESIS 2000).

Corrosion/ Irritation (Skin/ Eye) (Cr) Score (H, M or L): *H*

Because no corrosion/irritation toxicity data were identified for ethylenediamine phosphate, the components of the mixture were used as a surrogate. Ethylenediamine phosphate was assigned a score of High for corrosion and irritation based on animal studies showing the chemical to be corrosive and irritating.

Ethylenediamine

- *Dermal*: Application of an aqueous solution of 70% ethylenediamine to the skin of rabbits (# not reported) caused complete destruction within 6 to 12 minutes. A 10% solution of ethylenediamine in water caused a burn within 24 hours. A dermal NOEL of 0.1% was reported by the authors (UNEP 2001).
- *Ocular*: A 10% solution in water caused moderate corneal damage and extensive conjunctivitis. A 1% solution was essentially non-irritating. Species and number of animals tested were not reported (UNEP 2001).
- *Ocular*: Vapors ethylenediamine are mildly irritating to the eye after 10 seconds at 200 ppm while 400 ppm is intolerable. Species and number of test subjects were not reported (UNEP 2001).

Phosphoric acid

- *Dermal:* Several dermal studies have been completed on the compound. Phosphoric has been classified has irritating and corrosive at concentrations ranging from 35 to 100% (ESIS 2000)
- *Ocular:* Phosphoric acid was found to be not irritating to the eyes of rabbits following OECD guideline 405 at concentrations of 10 and 17% phosphoric acid (ESIS 2000).
- *Ocular:* Phosphoric acid is classified as potentially irritating to the eyes of humans (ESIS 2000).

Sensitization (Sn) Score (Skin and Respiratory) (H, M or L): *H*

Because no sensitization data were identified for ethylenediamine phosphate, the components of the mixture were used as a surrogate. Ethylenediamine phosphate was assigned a score of High for sensitization based on ethylenediamine testing positive for skin sensitization.

Ethylenediamine

- *Dermal*: Several skin sensitization studies have been reported for ethylenediamine including the following: guinea pig maximization test, draize test, repeated insult patch test, single injection adjuvant test, mouse optimization test, and a mouse ear swelling test. The test substance was confirmed to be sensitizing in the reported studies (UNEP 2001).
- *Respiratory/Dermal:* Ethylenediamine is associated with risk phrase 42/43. May cause sensitization by inhalation and skin contact (EINECS 2010).

Phosphoric acid

- *Dermal:* Phosphoric acid is classified as not sensitizing to humans. No other data was available for this study (ESIS 2000).

Systemic/ Organ (ST) Toxicity Score (includes organ effects and immunotoxicity) (H, M or L): *M*

Because no systemic/organ toxicity data were identified for ethylenediamine phosphate, the components of the mixture were used as a surrogate. Ethylenediamine phosphate was assigned a score of Moderate for systemic/organ toxicity based on repeat-dose analog studies suggesting renal toxicity in rodents.

Ethylenediamine

- A 13 week repeat dose oral toxicity study was conducted on F344 rats (10/sex/group). Concentrations of 0, 100, 200, 400, 600, and 800 mg/kg of ethylenediamine (purity not reported) were administered daily (5 days/week) by oral gavage for 13 weeks. Body weight gains were decreased in male and female rats administered 200 to 800 mg/kg. Several females in the 600 mg/kg and higher groups appeared to have smaller uterine horns and the 800 mg/kg group had smaller ovaries. Renal tubular lesions were noted in the 600 and 800 mg/kg groups. Male and female rats also exhibited bilateral cataracts in the 600 mg/kg group after 12 weeks. A LOAEL of 100 mg/kg was reported by the authors. This test study was reported to have followed OECD guideline 408 ―Subchronic Oral Toxicity – Rodent: 90-day Study" (UNEP 2001).
- A 13 week repeat dose oral toxicity study was conducted on B6C3F1 mice (10/sex/group). Concentrations of 0, 25, 50, 100, 200, and 400 mg/kg of

ethylenediamine (purity not reported) were administered daily (5 days/week) by oral gavage for 13 weeks. No body weight changes were observed. There were no treatment related gross lesions. Histopathologic changes were noted in the kidneys at 499 mg/kg. The kidney lesion was characterized by mild to moderate degeneration of the renal tubular epithelium. A NOEL of 200 mg/kg was reported by the authors. This test study was reported to have followed OECD guideline 408 ~~–~~Subchronic Oral Toxicity – Rodent: 90-day Study" (UNEP 2001).

Phosphoric acid

- No relevant data were identified for this phosphoric acid.

Ecotoxicity

Acute Aquatic (AA) Toxicity Score (H, M or L): L

Ethylenediamine phosphate was assigned a score of Low for acute aquatic toxicity based on LC_{50} values greater than 100 mg/L.

- An LC_{50} of > 100 mg/L was identified in fish (fish, 96 hour) (Fisk et al. 2003).
- ECOSAR – Ethylenediamine phosphate is designated to the aliphatic amines and neutral organics ECOSAR classes. The estimated L/EC_{50} values are 6266.691 mg/L (daphnid, 48 hr), and 320.865 mg/L (algae, 96 hr) (U.S. EPA 2009).

Chronic Aquatic (CA) Toxicity Score (H, M or L): H

Ethylenediamine phosphate was assigned a score of High for chronic aquatic toxicity based on an NOEC value < 0.1 mg/L.

- ECOSAR – The estimated ChV values are 2375.747 mg/L (fish, 96 hr), 0.082 mg/L (daphnid, 48 hr), and 723.378 mg/L (algae, 96 hr) (U.S. EPA 2009).

Environmental Fate

Persistence (P) Score (vH, H, M, or L): M

Ehtylenediamine phosphate was assigned a score of Moderate for persistence based on a soil half life of 30 days and water half life of 15 days.

- EPI Suite – BIOWIN model results indicate ethylenediamine phosphate is not readily biodegrade, and has a predicted degradation time of weeks. STP removal expected using BIOWIN/EPA Draft Method results indicate 75.06% total removal, with 74.44% due to biodegradation. Fugacity III modeling predicts 67.1% partitioning to soil with a half-life of 30 days, and 32.9% partitioning to water with a half-life of 15 days (U.S. EPA 2010).

Bioaccumulation (B) Score (vH, H, M, or L): L

Ethylenediamine phosphate was assigned a score of Low for bioaccumulation based on a BCF value less than 100.

- BCFBAF predicts a bioconcentration factor (BCF) of 3.162 L/kg wet-wt and a log K_{ow} of -4.54 (U.S. EPA 2010). BCF is used in instances where log Kow is <5.

Physical Properties

Explosivity (Ex) Hazard Rating (H, M or L): L

Because no explosivity data were identified for ethylenediamine phosphate, the components of the mixture were used as a surrogate. Ethylenediamine phosphate was assigned a score of Low for explosivity because no basis for concern was identified.

Ethylenediamine

- Ethylenediamine is stable (ScienceLab 2008).

Phosphoric acid

- Phosphoric acid is not explosive (ESIS 2000).

Flammability (F) Hazard Rating (H, M or L): L

Because no flammability data were identified for ethylenediamine phosphate, the components of the mixture were used as a surrogate. Ethylenediamine phosphate was assigned a score of Low for explosivity because no basis for concern was identified.

Ethylenediamine

- Ethylenediamine is flammable (ScienceLab 2008).

Phosphoric acid

- Phosphoric acid is not flammable (ESIS 2000).

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EPI Suite Results for Ethylenediamine Phosphate:

```
CAS Number: 14852-17-6
SMILES : NCCN(H)(H)(H)OP(=O)(O)O
CHEM   : 1,2-Ethanediamine, phosphate
MOL FOR: C2 H11 N2 O4 P1
MOL WT : 158.10
------------------------------ EPI SUMMARY (v4.00) --------------------------

 Physical Property Inputs:
    Log Kow (octanol-water):   ------
    Boiling Point (deg C)  :   ------
    Melting Point (deg C)  :   ------
    Vapor Pressure (mm Hg) :   ------
    Water Solubility (mg/L):   ------
    Henry LC (atm-m3/mole) :   ------

 Log Octanol-Water Partition Coef (SRC):
    Log Kow (KOWWIN v1.67 estimate) =  -4.54

Boiling Pt, Melting Pt, Vapor Pressure Estimations (MPBPVP v1.43):
    Boiling Pt (deg C):  480.00  (Adapted Stein & Brown method)
    Melting Pt (deg C):  90.27  (Mean or Weighted MP)
    VP(mm Hg,25 deg C):  6.06E-011  (Modified Grain method)
    VP (Pa, 25 deg C) :  8.07E-009  (Modified Grain method)
    Subcooled liquid VP: 2.58E-010 mm Hg (25 deg C, Mod-Grain method)
                       : 3.44E-008 Pa (25 deg C, Mod-Grain method)

 Water Solubility Estimate from Log Kow (WSKOW v1.41):
    Water Solubility at 25 deg C (mg/L):  1e+006
       log Kow used: -4.54 (estimated)
       no-melting pt equation used

 Water Sol Estimate from Fragments:
    Wat Sol (v1.01 est) =  1e+006 mg/L

 ECOSAR Class Program (ECOSAR v1.00):
    Class(es) found:
       Aliphatic Amines

 Henrys Law Constant (25 deg C) [HENRYWIN v3.20]:
   Bond Method :   9.03E-027  atm-m3/mole  (9.15E-022 Pa-m3/mole)
   Group Method:   Incomplete
 For Henry LC Comparison Purposes:
   User-Entered Henry LC:  not entered
   Henrys LC [via VP/WSol estimate using User-Entered or Estimated values]:
      HLC:  1.261E-017 atm-m3/mole  (1.277E-012 Pa-m3/mole)
      VP:   6.06E-011 mm Hg (source: MPBPVP)
      WS:   1E+006 mg/L (source: WSKOWWIN)

 Log Octanol-Air Partition Coefficient (25 deg C) [KOAWIN v1.10]:
  Log Kow used:  -4.54  (KowWin est)
  Log Kaw used:  -24.433  (HenryWin est)
      Log Koa (KOAWIN v1.10 estimate):  19.893
      Log Koa (experimental database):  None
```

```
 Probability of Rapid Biodegradation (BIOWIN v4.10):
   Biowin1 (Linear Model)         :   0.8261
   Biowin2 (Non-Linear Model)     :   0.8669
 Expert Survey Biodegradation Results:
   Biowin3 (Ultimate Survey Model):   2.8742  (weeks       )
   Biowin4 (Primary Survey Model) :   3.6629  (days-weeks  )
 MITI Biodegradation Probability:
   Biowin5 (MITI Linear Model)    :   0.3647
   Biowin6 (MITI Non-Linear Model):   0.2299
 Anaerobic Biodegradation Probability:
   Biowin7 (Anaerobic Linear Model):  0.6277
 Ready Biodegradability Prediction:   NO

Hydrocarbon Biodegradation (BioHCwin v1.01):
    Structure incompatible with current estimation method!

 Sorption to aerosols (25 Dec C)[AEROWIN v1.00]:
  Vapor pressure (liquid/subcooled):  3.44E-008 Pa (2.58E-010 mm Hg)
  Log Koa (Koawin est  ): 19.893
   Kp (particle/gas partition coef. (m3/ug)):
        Mackay model           :  87.2
        Octanol/air (Koa) model:  1.92E+007
   Fraction sorbed to airborne particulates (phi):
        Junge-Pankow model     :  1
        Mackay model           :  1
        Octanol/air (Koa) model:  1

 Atmospheric Oxidation (25 deg C) [AopWin v1.92]:
   Hydroxyl Radicals Reaction:
      OVERALL OH Rate Constant =  42.6481 E-12 cm3/molecule-sec
      Half-Life =     0.251 Days (12-hr day; 1.5E6 OH/cm3)
      Half-Life =     3.010 Hrs
   Ozone Reaction:
      No Ozone Reaction Estimation
   Fraction sorbed to airborne particulates (phi):
      1 (Junge-Pankow, Mackay avg)
      1 (Koa method)
    Note: the sorbed fraction may be resistant to atmospheric oxidation

 Soil Adsorption Coefficient (KOCWIN v2.00):
      Koc    :  6.269  L/kg (MCI method)
      Log Koc:  0.797       (MCI method)
      Koc    :  0.02976  L/kg (Kow method)
      Log Koc:  -1.526      (Kow method)

 Aqueous Base/Acid-Catalyzed Hydrolysis (25 deg C) [HYDROWIN v2.00]:
    Rate constants can NOT be estimated for this structure!

 Bioaccumulation Estimates (BCFBAF v3.00):
   Log BCF from regression-based method = 0.500 (BCF = 3.162 L/kg wet-wt)
   Log Biotransformation Half-life (HL) = -2.8838 days (HL = 0.001307 days)
   Log BCF Arnot-Gobas method (upper trophic) = -0.049 (BCF = 0.893)
   Log BAF Arnot-Gobas method (upper trophic) = -0.049 (BAF = 0.893)
        Kow log used: -4.54 (estimated)


 Volatilization from Water:
```

```
   Henry LC:  9.03E-027 atm-m3/mole  (estimated by Bond SAR Method)
   Half-Life from Model River: 8.153E+022  hours   (3.397E+021 days)
   Half-Life from Model Lake : 8.894E+023  hours   (3.706E+022 days)

 Removal In Wastewater Treatment:
   Total removal:               1.85  percent
   Total biodegradation:        0.09  percent
   Total sludge adsorption:     1.75  percent
   Total to Air:                0.00  percent
     (using 10000 hr Bio P,A,S)

 Removal In Wastewater Treatment:
   Total removal:              75.06  percent
   Total biodegradation:       74.44  percent
   Total sludge adsorption:     0.62  percent
   Total to Air:                0.00  percent
     (using Biowin/EPA draft method)

 Level III Fugacity Model:
          Mass Amount    Half-Life    Emissions
           (percent)        (hr)       (kg/hr)
   Air       6.65e-016       6.02         1000
   Water     32.9            360          1000
   Soil      67.1            720          1000
   Sediment  0.0688          3.24e+003    0
     Persistence Time: 622 hr
```

ECOSAR Results for Ethylenediamine Phosphate:

```
SMILES : NCCN(H)(H)(H)OP(=O)(O)O
CHEM   : 1,2-Ethanediamine, phosphate
CAS Num: 014852-17-6
ChemID1:
ChemID2:
ChemID3:
MOL FOR: C2 H11 N2 O4 P1
MOL WT : 158.10
Log Kow: -4.54  (KowWin estimate)
Melt Pt:
Wat Sol: 1E+006 mg/L  (WskowWin estimate)

ECOSAR v1.00 Class(es) Found
------------------------------
Aliphatic Amines
                                                        Predicted
ECOSAR Class                   Organism               Duration  End Pt   mg/L (ppm)
===========================  ===================  ========  ======   ==========
Aliphatic Amines           : Fish                 96-hr     LC50     2.4e+005
Aliphatic Amines           : Daphnid              48-hr     LC50     6266.691
Aliphatic Amines           : Green Algae          96-hr     EC50     320.865
Aliphatic Amines           : Fish                           ChV      2375.747
Aliphatic Amines           : Daphnid                        ChV      0.082
Aliphatic Amines           : Green Algae                    ChV      723.378
Aliphatic Amines           : Fish  (SW)           96-hr     LC50     2.42e+005
Aliphatic Amines           : Mysid Shrimp (SW)    96-hr     LC50     6979.869
Aliphatic Amines           : Green Algae (SW)     96-hr     EC50     322.587
```

```
Aliphatic Amines         : Fish  (SW)                ChV      2375.747
Aliphatic Amines         : Mysid Shrimp (SW)           ChV        0.082
Aliphatic Amines         : Green Algae (SW)           ChV      564.342
==========================  ==================  ========  ======   ==========
Neutral Organic SAR       : Fish              96-hr     LC50     4.2e+007 *
(Baseline Toxicity)       : Daphnid           48-hr     LC50     1.1e+007 *
                     : Green Algae        96-hr    EC50    3.23e+005
                     : Fish                      ChV      4.6e+006 *
                     : Daphnid                    ChV     3.19e+005
                     : Green Algae                 ChV     35379.375
 Note:  * = asterisk designates: Chemical may not be soluble  enough to measure this predicted effect.

Aliphatic Amines:
----------------
  For Fish 96-hr LC50: For aliphatic amines with log Kow greater than 7.0, a test duration of greater than
96 hrs may be required for proper expression of toxicity. Also, if the toxicity value obtained by the use
of this equation exceeds the water solubility (measured or estimated), mortalities greater than 50% would
not be expected in a saturated solution during an exposure period of 96 hrs.

  For Daphnid 48-hr LC50: For aliphatic amines with log Kow greater than
5.0, a test duration of greater than 48 hrs may be required for proper
expression of toxicity. Also, if the toxicity value obtained by the use
of this equation exceeds the water solubility (measured or estimated),
significant mortalities would not be expected in a saturated solution
during an exposure period of 48 hrs.

  For Green Algae Acute Toxicity Values: If the log Kow of the chemical is
greater than 7, or if the compound is solid and the EC50 exceeds the water
solubility by 10X, no effects at saturation are predicted for these endpoints.

  For Mysid Shrimp Acute Toxicity Values: If the log Kow of the chemical is
greater than 6, or if the compound is solid and the EC50 exceeds the water
solubility by 10X, no effects at saturation are predicted for these endpoints.

  For Fish and Daphnid Chronic Toxicity Values: If the log Kow of the chemical
is greater than 8.0, or if the compound is solid and the ChV exceeds the water
solubility by 10X, no effects at saturation are predicted for these endpoints.

  For Green Algae Chronic Toxicity Values: If the log Kow of the chemical
is greater than 7.0, or if the compound is solid and the ChV exceeds the water
solubility by 10X, no effects at saturation are predicted for these endpoints.

ECOSAR v1.00 SAR Limitations:
----------------------------
Maximum LogKow: 6.0 (Fish, Mysid LC50)
Maximum LogKow: 5.0 (Daphnid LC50)
Maximum LogKow: 7.0 (Green Algae EC50)
Maximum LogKow: 8.0 (Fish, Daphnid ChV)
Maximum LogKow: 7.0 (Green Algae ChV)
Maximum Mol Wt: 1000
 Baseline Toxicity SAR Limitations:--------------------------------
Maximum LogKow: 5.0 (Fish 96-hr LC50; Daphnid LC50)
Maximum LogKow: 6.4 (Green Algae EC50)
Maximum LogKow: 8.0 (ChV)
Maximum Mol Wt: 1000
```

Ethylenediamine Phosphate Green Screen Evaluation Prepared By:

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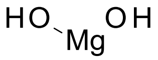
APPENDIX IX F: GREEN SCREEN FOR MAGNESIUM HYDROXIDE (CAS #1309-42-8)[15]

Also Called: 200-06H, Alcanex NHC 25, Asahi Glass 200-06, Baschem 12, CCRIS 3342, Combustrol 500, DP 393, DSB 100, Duhor, Duhor N, EINECS 215-170-3, Ebson RF, FloMag H, FloMag HUS, HSDB 659, Hydro-mag MA, Hydrofy G 1.5, Hydrofy G 2.5, Hydrofy N, KX 8S(A), KX 8S(B), Ki 22-5B, Kisuma 4AF, Kisuma 5, Kisuma 5A, Kisuma 5B, Kisuma 5B-N, Kisuma 5BG, Kisuma 5E, Kisuma 78, Kisuma S 4, Kyowamag F, Lycal 96 HSE, Mag Chem MH 10, Magmesia hydrate, MagneClear 58, Magnesia magma, Magnesia, [milk of], Magnesiamaito, Magnesium dihydroxide, Magnesium hydroxide, Magnesium hydroxide ($Mg(OH)_2$), Magnesium hydroxide gel, Magnesium oxide ($Mg(OH)_2$), Magnesium(II) hydroxide, Magnifin H 10, Magox, Marinco H, Marinco H 1241, Martinal VPF 8812, Milk of magnesia, Milmag, Mint-O-Mag, Nemalite, Oxaine M, Phillips Magnesia Tablets, Phillips Milk of Magnesia Liquid, Reachim, S/G 84, Star 200, UNII-NBZ3QY004S, Versamag

Chemical Structure of Magnesium Hydroxide:



***Note:** Data gaps for this chemical were addressed by using other structurally similar magnesium salts such as magnesium chloride, magnesium lactate, and magnesium citrate. These chemicals in particular were selected due to the fact they are expected to dissociate in stomach acid and because they have been used in other risk assessments as surrogates for magnesium hydroxide (NAS 2000, U.S. EPA 2008).

For Inorganic Chemicals:
Define Form & Physiochemical Properties

7. Particle size (e.g. silica of respirable size) – n/a
8. Structure (e.g. amorphous vs. crystalline) – n/a
9. Mobility (e.g. Water solubility, volatility) – 0.009 g/L at 18°C (Hodgman 1959); 0.04 g/L at 100°C (Hodgman 1959)

Identify Applications/Functional Uses: Flame retardant

Green Screen Rating[16]: Magnesium hydroxide was assigned a Benchmark Score of 2 based on a very High persistence (P) rating and a Moderate corrosion (Cr) rating (2c).

Green Screen (Version 1.0) Levels of Concern for Magnesium Hydroxide														
Human – Tier 1					**Human – Tier 2**				**Eco**		**Fate**		**Physical**	
C	**M**	**R/D**	**ED**	**N**	**AT**	**Cr**	**Sn**	**ST**	**AA**	**CA**	**P**	**B**	**Ex**	**F**
L	**L**	**L**	nd	*L*	**L**	**M**	*L*	**M**	**L**	**L**	**vH**	**L**	**L**	**L**

*Endpoints in italics were assigned using estimated values and professional judgment (Structure Activity Relationships).

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[15] CPA recommends independent third-party validation of all Green Screen assessments. No independent third-party validation has been done for this assessment . Companies may not make marketing claims based on a Green Screen assessment that has not undergone an independent validation.

[16] For inorganic chemicals with low human and ecotoxicity across all hazard endpoints and low bioaccumulation, persistence alone will not be deemed problematic. Inorganic chemicals that are only persistent will be evaluated under the criteria for Benchmark 4.

Transformation Products and Ratings:
Identify relevant fate and transformation products (i.e., dissociation products, transformation products, valence states) **and/or moieties of concern**[17]

Life Cycle Stage	Transformation Pathway	Transformation Products	CAS #	Green Screen Rating
End of Life	Hydrolysis	Water	7732-18-5	4
End of Life	Hydrolysis	Magnesium	7439-95-4	Not present on the Red List of Chemicals (CPA 2009)
End of Life	Hydrolysis	Hydrogen peroxide	7722-84-1	Not present on the Red List of Chemicals (CPA 2009)

*The above transformation products were screened against the CPA's table of Red List chemicals; none were found.

Introduction

Magnesium hydroxide is commonly used as an antacid and is the active ingredient in the laxative, milk of magnesia (NAS 2000). Additionally, it is used as a residual fuel-oil additive, an alkali drying agent in food, a color-retention agent, and is an ingredient of tooth (NAS 2000). $Mg(OH)_2$ is used as a flame retardant (FR) in commercial furniture applications in the United States and in commercial and residential furniture in the United Kingdom (Fire Retardant Chemicals Association 1998). The stability of $Mg\ (OH)_2$ at temperatures above 300°C allows it to be incorporated into several polymers (IPCS 1997).

Human Health – Tier 1

Carcinogenicity (C) Score (H, M or L): L

Magnesium hydroxide was assigned a score of Low for carcinogenicity due to findings from several animal studies.

- Not listed as a known carcinogen by IARC, NTP, U.S. EPA, or CA Prop 65.
- Oncologic results predict the hazard rating for carcinogenicity for magnesium hydroxide to be low (OncoLogic 2005).
- The incidence of all cancers among 2,391 Norwegian males who worked between 1951 and 1974 in a factory producing magnesium metal was not significantly increased when compared with cancer incidence for the Norwegian nation population of the same age. The number of cases of lip as well as stomach and lung cancers was significantly increased. Workers in this study were also

---

[17] A moiety is a discrete chemical entity that is a constituent part or component of a substance. A moiety of concern is often the parent substance itself for organic compounds. For inorganic compounds, the moiety of concern is typically a dissociated component of the substance or a transformation product.

exposed to magnesium oxide dust, coal dust, chlorine gas, hydrochlorine aerosols, chlorinated aromatics, and sulphur dioxide. Therefore, it is not possible to determine whether exposure to magnesium dust alone is responsible for the observed elevations in cancer incidence (Heldaas 1989).

- Exposure of male Wistar rats to short (4.9x0.31 mm) or long (12x0.44) $MgSO_4 \cdot 3H_2O$ filaments by inhalation (6 hours per day, 5 days per week for 1 year) was not associated with an increase in the incidence of any tumor types in animals sacrificed 1 day or 1 year after cessation of exposure. One year after exposure, one pulmonary adenoma was observed in animals that had been exposed to long filaments for 3 weeks and none in controls. One year after exposure, neoplastic lesions were observed in control animals and short- and long-filament treated rats that had been exposed for 1 year. Two pulmonary adenomas were observed in the exposed animals and one in control animals. No hepatocellular adenomas or carcinomas occurred in controls, one hepatocellular adenoma was found in the long-filament group, and one hepatocellular carcinoma was found in the short-filament group, respectively (Hori 1994).
- Mice fed 0.5% or 2% of aqueous $MgCl_2$ in their diet for 96 weeks (68, or 336 mg/kg-day for males; 87 or 470 mg/kg-day for females) showed no significant change in the incidence of malignant lymphoma and leukemia. Dose-related increases in incidence of malignant lymphoma and leukemia occurred in male mice (controls, five of 50; low dose, seven of 50; high dose, eleven of 50), but not in females (controls, nine of 49; low dose, 17 of 50; high dose, 11 of 50). The incidence of hepatocellular carcinomas in male mice was decreased in a dose-related manner (controls, 13 of 50; low dose, six of 50; high dose, four of 50) and the incidence in high-dose males was significantly different from that in controls. Toxicity in female mice (i.e., decreased body weight) suggests that the study was conducted at or near the maximum tolerated dose (MTD) for females (Kurata 1989).
- Several studies in rats have shown that dietary $Mg(OH)_2$ can protect against chemically induced bowel carcinogenesis by suppressing hyperproliferation of the colon epithelium. Dietary levels of 250 ppm $Mg(OH)_2$ inhibited the incidence of colon adenoma and adenocarcinoma in rats given carcinogens methylazoxymethanol acetate (MAM acetate) or 1, 2-dimethylhydrazine (Tanaka 1989; Morishita 1991; Mori 1993). Administration of $Mg(OH)_2$ in the diet and the bowel carcinogen cholic acid reduced cell proliferation in bowel tissue (Wang 1993). Dietary $Mg(OH)_2$ also prevented the expression of *c-myc* gene in colon mucosa cells of MAM acetate-treated rats (Wang 1993).
- The subcommittee concludes that $Mg(OH)_2$ is not likely to be carcinogenic to humans by the oral route. No adequate data are available to assess the carcinogenicity of $Mg(OH)_2$ by the dermal or inhalation or routes of exposure (NAS 2000).

Mutagenicity (M) and Genotoxicity Score (H, M or L): L

Magnesium hydroxide was assigned a score of Low for mutagenicity based on negative results from several genotoxocity assays.

- $MgCl_2$ was judged to be a non-mutagen in the Ames assay when tested with and without metabolic activation and it did not induce chromosomal aberrations in

Chinese hamster fibroblast cells in vitro (Ishidate 1984). Chromatid gaps, breaks, and exchanges were observed in Chinese hamster lung fibroblasts treated with $MgCl_2$ at concentrations of 8.0 and 12.0 mg/ml but not at or below concentrations of 4 mg/mL (Ashby and Ishidate 1986). Since positive results occurred at only high concentrations, the authors suggest that the clastogenic effects observed may be an artifact induced by hypertonic solutions. $MgCl_2$ did not induce mutations in mouse lymphoma L5178/TK+/− cells at concentrations of 5.7–18.1 mg Mg^{2+}/ml (Amacher and Paillet 1980). MgSO4 was not mutagenic in Salmonella typhimurium (strains TA100, TA1535) and Escherichia coli WP2 uvrA at concentrations of 313–5,000 mg/plate (Oguma 1998). MgSO4 was not mutagenic in Salmonella strain TA98 tested without metabolic activation and strain TA1537 tested with metabolic activation at a concentration of 156–5,000 mg/plate (Oguma 1998).

Reproductive (R) and Developmental (D) Toxicity Score (H, M or L): L
Magnesium hydroxide was assigned a score of Low for reproductive and developmental toxicity based on the results from one animal study and one study in humans.

- No maternal or reproductive effects were observed in a 10 day (GD 6-15) oral reproductive/developmental study on rats using $MgCl_2$. The authors of the study determined the NOAEL to be >96 mg/kg/day for Mg^{2+} (NAS 2000).
- A repeated dose/developmental (3rd trimester) study on humans produced no effect on newborns except slightly increased body weight and hypermagnesiumemia. Cord serum magnesium levels reported to be 70-100% of maternal levels (potentially causing neurological depression in neonate, characterized by respiratory depression, muscle weakness, decreased reflexes). Prolonged magnesium treatment during pregnancy may be associated with maternal and fetal hypocalcemia and adverse effects on fetal bone mineralization (HSDB 2003).

Endocrine Disruption (ED) Score (H, M or L): nd

- Not listed as a potential endocrine disruptor on the EU Priority List of Suspected Endocrine Disruptors.
- Not listed as a potential endocrine disruptor on the OSPAR List of Chemicals of Possible Concern.
- Not listed as a potential endocrine disruptor on the Red List of Chemicals (CPA 2009).
- No other relevant endocrine disruption data could be identified for magnesium hydroxide.

Neurotoxicity (N) Score (H, M or L): *L*
Magnesium hydroxide was assigned a score of Low for neurotoxicity based on professional judgement.

- Not classified as a developmental neurotoxicant (Grandjean and Landrigan 2006).
- Not listed as a potential neurotoxicant on the Red List of Chemicals (CPA 2009).
- Magnesium hydroxide is expected to be of low hazard for neurotoxicity based on professional judgment (U.S. EPA 2008).

Human Health – Tier 2

Acute Mammalian (AT) Toxicity Score (H, M or L): L

Magnesium hydroxide was assigned a score of Low for acute mammalian toxicity based on oral LD_{50} values greater than 2,000 mg/kg-bw. This score is based on data from one route of exposure in two different species of animals.

- *Oral*: An LD_{50} of 8,500 mg/kg was determined in the rat (Lewis 2000).
- *Oral*: An LD_{50} of 8,500 mg/kg was determined in the mouse (Lewis 2000)

Corrosion/Irritation (Skin/ Eye) (Cr) Score (H, M or L): M

Magnesium hydroxide was assigned a score of Moderate for corrosion/irritation based on the substance being moderately irritating to the eyes of rabbits.

- *Dermal*: No relevant data were identified for magnesium hydroxide.
- *Ocular*: Moderately irritating to rabbit eyes (IUCLID 2000).
- *Ocular*: Administration of milk of magnesia twice a day for 3-4 days caused damage to corneal epithelium of rabbit eyes; however, effects disappeared within 2-3 days. No additional details were provided (HSDB 2003).

Sensitization (Sn) Score (Skin and Respiratory) (H, M or L): *L*

Magnesium hydroxide was assigned a score of Low for sensitization based on professional judgment.

- Magnesium hydroxide is not expected to cause skin sensitization based on professional judgment. No other details were provided (U.S. EPA 2008).

Systemic/ Organ (ST) Toxicity Score (includes organ effects and immunotoxicity) (H, M or L): M

Magnesium hydroxide was assigned a score of Moderate for systemic/organ toxicity based on suggestive animal studies.

- No human studies were found that investigated the toxic effects of $Mg(OH)_2$ following inhalation exposure. Exposure of male Wistar rats to short (4.9x0.31 mm) or long (12x0.44 mm) $MgSO_4/5Mg(OH)_2{\cdot}3H_2O$ filaments inhalation, 6 hours per day, 5 days per week for up to a year was associated with a slight increase in the incidence of pulmonary lesions 1 year after cessation of exposure. A year after cessation of exposure, histopathological examination of treated animals revealed a slight increase in segmental calcification of the pulmonary artery and thickening of the lung pleura in rats exposed to either short or long filaments for 4 week or 1 year. Differences between exposed and unexposed animals were statistically significant. No significant differences in body, lung, liver, kidney, or spleen weights were detected between animals sacrificed 1 day or 1 year after a 1 year exposure to short or long filaments. No significant differences in survival were observed between animals sacrificed 1 day or 1 year after a 1 year exposure to short or long filaments (Hori 1994).
- In its review of clinical studies, the Institute of Medicine (IOM 1997) concluded that Mg^{2+} in the diet is never high enough to cause adverse effects. The IOM set a –tolerable upper intake level" (TUL) for the ingestion of magnesium (Mg^{2+}) supplements of 5 mg/day for anyone over 1 year old. The TUL was based on the

approximate no-observed-adverse-effects level (NOAEL) for osmotic diarrhea in humans reported by Marken (1989), Fine (1991), Ricci (1991), and Bashir (1993). Five of the six patients reported epigastric burning or distension and two reported diarrhea.

- Decreased body weight was found to be the critical effect in B6C2F1 mice fed diets containing 0%, 0.3%, 0.6%, 1.25%, 2.5%, or 5% $MgCl_2 \cdot 6H_2O$ for 13 weeks. Intake of Mg^{2+} added to the diet was calculated to be 73, 146, 322, 650, or 1,368 mg/kg-day in treated males and 92, 190, 391, 817, and 1,660 mg/kg-day in treated females (the amount of magnesium in the basal diet was not provided). The 5% treatment group of both sexes showed a significant decrease in weight gain (15% in males and 10% in females). Males in the 2.5 and 5% group exhibited an increased incidence of renal tubular vacuolation. The authors determined that the LOAEL for this study was 650 mg/kg-day (Tanaka 1994).
- Decreased body weight and increased renal vacuolation were observed in male, but not female B6C3F1 mice fed a diet that contained 5% $MgCl_2 \cdot 6H_2O$ (Mg^{2+} at 840 mg/kg-day) for 13 weeks. No treatment-related effects were reported for male and female mice fed a diet containing 0, 0.3, 0.6, 1.25 or 2.5% $MgCl_2 \cdot 6H_2O$ for 13 weeks. The NOAEL for Mg^{2+} in this study was determined to be 587 mg/kg-day for females and 420 mg/kg-day for males (Kurata 1989).
- Decreased body weight gain (about 25% at termination of the exposure) and increases in relative brain, heart, and kidney weights compared with controls were observed in female B6C3F1 mice fed diets for 96 weeks that contained 2% $MgCl_2 \cdot 6H_2O$ (470 mg Mg^{2+}/kg-day). No treatment-related effects were observed in male mice fed diets that contained 0.5% or 2% of $MgCl_2 \cdot 6H_2O$ (68 or 336 mg/kg-day) or female mice fed diets that contained 0.5% of $MgCl_2 \cdot 6H_2O$ (87 mg/kg-day) for 96 weeks. Histopathological examination after 104 weeks of exposure revealed no treatment-related changes. Urinary, hematological, and clinical chemistry parameters and histopathological measures were not affected by treatment, except for a significant increase in serum albumin in high-dose females. Survival rates were comparable between treated and control animals. The LOAEL for this study is 470 mg/kg-d based on the treatment-related effects in high-dose female mice (Kurata 1989).

Ecotoxicity

Acute Aquatic (AA) Toxicity Score (H, M or L): L

Magnesium hydroxide was assigned a score of Low for acute aquatic toxicity based on LC_{50} values greater than 100 mg/L.

- An LC_{50} of 1,110 mg/L was estimated in fish (species not specified) (fish, 96 hour) from the measured LC_{50}s for $MgCl_2$ and $MgSO_4$, modified by a molecular weight adjustment for $Mg(OH)_2$ (Mount 1997).
- An LC_{50} of 648 mg/L was estimated in daphnia (species not identified) (daphnid, 48 hour) from the measured LC_{50}s for $MgCl_2$ and $MgSO_4$, modified by a molecular weight adjustment for $Mg(OH)_2$ (Mount 1997; Biesinger and Christensen 1972).

- An EC_{50} of 2,111 mg/L was estimated in green algae (species not identified) (green algae, 96 hour) by using an acute to chronic ratio of 4 (U.S. EPA 2008).

Chronic Aquatic (CA) Toxicity Score (H, M or L): L

Magnesium hydroxide was assigned a score of Low for chronic aquatic toxicity based on ChV values greater than 10 mg/L.

- A ChV of 403 mg/L was estimated in fish (species not identified) (fish, time not identified) using an acute to chronic ratio of 3.3. This ratio is for daphnids and has not been validated for use with fish (U.S. EPA 2008).
- A ChV of 197 mg/L was estimated in daphnia (species not identified, length of time not identified) from the measured ChV for Mg^{2+} ion, modified by a molecular weight adjustment for $Mg(OH)_2$ (Suter 1996).
- A ChV of 528 mg/L was estimated in green algae (species not identified, length of time not identified) from the measured NOEC and LOEC for $MgSO_4$, modified by a molecular weight adjustment for $Mg(OH)_2$ (ECOTOX Database undated).

Environmental Fate

Persistence (P) Score (vH, H, M, or L): vH

Magnesium hydroxide was assigned a score of very High for persistence based on its inability to biodegrade in the environment.

- As a fully oxidized inorganic material, magnesium hydroxide is not expected to biodegrade, oxidize in air, or undergo hydrolysis under environmental conditions. Magnesium hydroxide does not absorb light at environmentally relevant wavelengths and is not expected to photolyze. No degradation processes for magnesium hydroxide under typical environmental conditions were identified. Chemical is identified as recalcitrant (U.S. EPA 2008).

Bioaccumulation (B) Score (vH, H, M, or L): L

Magnesium hydroxide was assigned a score of Low for bioaccumulation based on a BCF value less than 500.

- Magnesium hydroxide is not expected to be bioaccumulative based on an estimated BCF of <500 (U.S. EPA 2008).

Physical Properties

Explosivity (Ex) Hazard Rating (H, M or L): L

Magensium hydroxide was assigned a score of Low for explosivity because no basis for concern was identified.

- Magnesium hydroxide is not explosive (IUCLID 2000).

Flammability (F) Hazard Rating (H, M or L): L

Magensium hydroxide was assigned a score of Low for fammability because no basis for concern was identified.

- Magnesium hydroxide is not flammable (IUCLID 2000).

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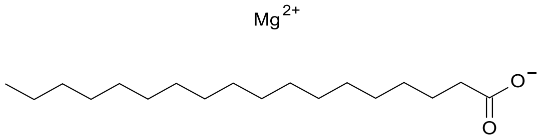
APPENDIX IX G: GREEN SCREEN FOR MAGNESIUM STEARATE (CAS #557-04-0)[18]

Also Called: Magnesium octadecanoate, Magnesium stearate, Magnesium stearate [JAN], Octadecanoic acid, magnesium salt, AI3-01638, Dibasic magnesium stearate, EINECS 209-150-3, HSDB 713, Magnesium distearate, Magnesium octadecanoate, Magnesium stearate, NP 1500, NS-M (salt), Octadecanoic acid, magnesium salt, Petrac MG 20NF, SM 1000, SM-P, Stearic acid, magnesium salt, Synpro 90, Synpro Magnesium Stearate 90, UNII-70097M6I30

Chemical Structure of Magnesium Stearate:



For Inorganic Chemicals:
Define Form & Physiochemical Properties

10. Particle size (e.g. silica of respirable size) – n/a
11. Structure (e.g. amorphous vs. crystalline) – Fine, white powder (HSDB 2009)
12. Mobility (e.g. Water solubility, volatility) – Not soluble in water (NIOSH 1994); soluble in hot alcohol (Mallinckodt Chemicals 2009).

Identify Applications/Functional Uses: Flame retardant

Green Screen Rating[19]: Magnesium stearate was assigned a Benchmark Score of 2 based on its High persistence (P) and Moderate irritation/corrosion (Cr) and systemic/organ toxicity (ST) (2c).

Green Screen (Version 1.0) Levels of Concern for Magnesium Stearate														
Human – Tier 1					Human – Tier 2				Eco		Fate		Physical	
C	M	R/D	ED	N	AT	Cr	Sn	ST	AA	CA	P	B	Ex	F
L	L	L	nd	nd	L	M	L	M	*L*	*M*	H	L	M	H

*Endpoints in italics were assigned using estimated values and professional judgment (Structure Activity Relationships).

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[18] CPA recommends independent third-party validation of all Green Screen assessments. No independent third-party validation has been done for this assessment . Companies may not make marketing claims based on a Green Screen assessment that has not undergone an independent validation.

[19] For inorganic chemicals with low human and ecotoxicity across all hazard endpoints and low bioaccumulation, persistence alone will not be deemed problematic. Inorganic chemicals that are only persistent will be evaluated under the criteria for Benchmark 4.

Transformation Products and Ratings:

Identify relevant fate and transformation products (i.e., dissociation products, transformation products, valence states) **and/or moieties of concern**[20]

Life Cycle Stage	Transformation Pathway	Transformation Products	CAS #	Green Screen Rating
End of Life	Dissociation	Magnesium	7439-95-4	Not present on the Red List of chemicals (CPA 2009)
End of Life	Dissociation	Octadecanoic acid	57-11-4	Not present on the Red List of chemicals (CPA 2009)
End of Life	Combustion	Carbon monoxide	630-08-0	Reproductive/developmental toxicant, neurotoxicant (CPA 2009)
End of Life	Combustion	Carbon dioxide	124-38-9	Not present on the Red List of chemicals (CPA 2009)
End of Life	Combustion	Magnesium oxide	1309-48-4	Not present on the Red List of chemicals (CPA 2009)

*The above transformation products were screened against the CPA's table of Red List chemicals (CPA 2009).

Introduction

Magnesium stearate is used as a filler material and binder in drug tablets and as an emulsification agent in cleansing products and cosmetics (HSDB 2009). Because the chemical is commonly used in pharmaceuticals, it has been listed as Generally Recognized as Safe (GRAS) by the FDA (U.S. FDA 2010).

The National Institute of Occupational Safety and Health have established a threshold limit value (TLV) for magnesium stearate of 10 mg/m^3 and the Occupational Safety and Health Administration assigned a permissible exposure limit (PEL) of 15 mg/m^3 (NIOSH 1994, Mallinckrodt Chemicals 2009).

Human Health – Tier 1

Carcinogenicity (C) Score (H, M or L): L

Magnesium stearate was assigned a score of Low for carcinogenicity because no basis for concern was identified.

- Not listed as a known carcinogen by IARC, NTP, U.S. EPA or CA Prop 65.
- A4- Not classifiable as a human carcinogen (HSDB 2009).

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[20] A moiety is a discrete chemical entity that is a constituent part or component of a substance. A moiety of concern is often the parent substance itself for organic compounds. For inorganic compounds, the moiety of concern is typically a dissociated component of the substance or a transformation product.

Mutagenicity (M) and Genotoxicity Score (H, M or L): L
Magnesium stearate was assigned a score of Low for mutagenicity based on a negative Ames assay results.

- Magnesium stearate tested negative in an Ames assay (concentrations and strains not reported) both with and without metabolic activation (Litton Bionetics 1976).

Reproductive (R) and Developmental (D) Toxicity Score (H, M or L): L
Magnesium stearate was assigned a score of Low for reproductive and developmental toxicity based on negative test results in rabbits.

- Magnesium stearate did not induce developmental effects in orally treated pregnant rabbits (no other detail provided) (U.S. EPA 2009b).
- A vehicle containing 5.5% magnesium stearate did not induce any teratogenic effects at doses of 2.5 mg/kg when administered orally to pregnant rabbits (no other details provided) (Gottschewshi 1967).

Endocrine Disruption (ED) Score (H, M or L): nd

- Magnesium stearate is not listed as a potential endocrine disruptor on the EU Priority List of Suspected Endocrine Disruptors.
- Magnesium stearate is not listed as a potential endocrine disruptor on the OSPAR List of Chemicals of Possible Concern.
- Magnesium stearate is not listed as a potential endocrine disruptor on the Red List of Chemicals (CPA 2009).

Neurotoxicity (N) Score (H, M or L): nd

- Magnesium stearate is not classified as a developmental neurotoxicant (Grandjean and Landrigan 2006).
- Magnesium stearate is not listed as a potential neurotoxicant on the Red List of Chemicals (CPA 2009).

Human Health – Tier 2

Acute Mammalian (AT) Toxicity Score (H, M or L): L
Magnesium stearate was assigned a score of Low for acute mammalian toxicity based on an oral LD_{50} greater than 2,000 mg/kg-bw. Data is based on studies from one route of exposure in one species of animals.

- *Oral*: An LD_{50} of >10,000 mg/kg-bw was established in the rat (U.S. EPA 2009b).

Corrosion/ Irritation (Skin/ Eye) (Cr) Score (H, M or L): M
Magnesium stearate was assigned a score of Moderate for corrosion and irritation based on conflicting results.

- *Dermal*: Magnesium stearate is a slight skin irritant (Science Lab 2008).
- *Ocular*: Magnesium stearate is slightly hazardous in the case of eye contact (Natural Sourcing 2009).

Sensitization (Sn) Score (Skin and Respiratory) (H, M or L): L
Magnesium stearate was assigned a score of Low for sensitization based on negative test results.

- Magnesium stearate is does not induce dermal sensitization (no other details provided) (U.S. EPA 2009b).

Systemic/ Organ (ST) Toxicity Score (includes organ effects and immunotoxicity) (H, M or L): M
Magnesium stearate was assigned a score of Moderate for systemic/organ toxicity based on results from animal studies.

- Magnesium stearate was fed to groups of 20 male and 20 female rats (strain not reported) at levels of 0, 5, 10 and 20% in a semisynthetic diet for 3 months. Decreased weight gain was found in males in the 20% group. Urolithiasis was found in 8 males and in 7 females in the same group. Reduced relative liver weight was seen in males in the 10% and in the 20% groups, and an increased amount of iron was found in the livers of the 20% group. Nephrocalcinosis was reduced in females in the 20% group. In this experiment the no-effect-level is estimated to be 5% magnesium stearate in the diet, corresponding to 2,500 mg/kg bw/day (Sondergaard 1980).
- Magnesium stearate did not induce any adverse effects in rats when treated orally with 500 mg/kg/day for 13 months (no other details provided) (U.S. EPA 2009b).
- Magnesium stearate targets the liver and skin (Science Lab 2008).
- Repeated or prolonged exposure to magnesium stearate can produce target organs damage (Science Lab 2008).
- Grossly excessive and chronic inhalation of the dust may cause a progressive chemical pneumonitis, cyanosis, and pulmonary edema (Mallinckrodt Chemicals 2009).

Ecotoxicity

Acute Aquatic (AA) Toxicity Score (H, M or L): *L*
Magnesium stearate was assigned a score of Low for acute aquatic toxicity based on professional opinion.

- ECOSAR was unable to predict E/LC$_{50}$ values for magnesium stearate due to its low solubility.
- Magnesium stearate is classified as a neutral organic.

Chronic Aquatic (CA) Toxicity Score (H, M or L): *M*
Magnesium stearate was assigned a score of Moderate for chronic aquatic toxicity based on GHS's recommendation.

- ECOSAR was unable to predict ChV values for magnesium stearate due to its low solubility.

Environmental Fate

Persistence (P) Score (vH, H, M, or L): H

Magnesium stearate was assigned a score of High for persistence based on its inability to biodegrade and a half life between 60 and 180 days in soil.

- The products of degradation are more toxic than the parent compound (Science Lab 2008).
- EPI Suite – BIOWIN model results indicate magnesium stearate is not readily biodegradable, and has a predicted degradation time of days to month. STP removal expected using BIOWIN/EPA Draft Method results indicate approximately 99% total removal, with approximately 37% due to biodegradation. Fugacity III modeling predicts approximately 84% partitioning to soil with a half-life of 75 days, and approximately 16% partitioning to water with a half-life of 38 days (U.S. EPA 2010).

Bioaccumulation (B) Score (vH, H, M, or L): L

Magnesium stearate was assigned a score of Low for bioaccumulation based on a BAF less than 500.

- BCFBAF predicts a bioaccumulation factor (BAF) of 7.079 and a log K_{ow} of 14.44 (U.S. EPA 2009a).

Physical Properties

Explosivity (Ex) Hazard Rating (H, M or L): M

Magnesium stearate was assigned a score of Moderate for explosivity based on its ability to explode when in powder form.

- Dust explosion possible if in powder or granular form and mixed with air (NIOSH 1994).

Flammability (F) Hazard Rating (H, M or L): H

Magnesium stearate was assigned a score of High for flammability based on it being combustible.

- Magnesium stearate is spontaneously combustible (HSDB 2009).
- Magnesium stearate may be combustible at high temperatures (Science Lab 2008).

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EPI Suite Results for Magnesium Stearate:

```
CAS Number: 557-04-0
SMILES : [Zn](OC(=O)CCCCCCCCCCCCCCCCC)OC(=O)CCCCCCCCCCCCCCCCC
CHEM   : Zinc stearate
MOL FOR: C36 H70 O4 Zn1
MOL WT : 632.35
------------------------------ EPI SUMMARY (v4.00) --------------------------
 Physical Property Inputs:
    Log Kow (octanol-water):   ------
    Boiling Point (deg C)  :   ------
    Melting Point (deg C)  :   ------
    Vapor Pressure (mm Hg) :   ------
    Water Solubility (mg/L):   ------
    Henry LC (atm-m3/mole) :   ------

 Log Octanol-Water Partition Coef (SRC):
    Log Kow (KOWWIN v1.67 estimate) =  14.44

Boiling Pt, Melting Pt, Vapor Pressure Estimations (MPBPVP v1.43):
    Boiling Pt (deg C):  675.43  (Adapted Stein & Brown method)
    Melting Pt (deg C):  294.55  (Mean or Weighted MP)
    VP(mm Hg,25 deg C):  2.71E-015  (Modified Grain method)
    VP (Pa, 25 deg C) :  3.61E-013  (Modified Grain method)
    MP  (exp database):  250 deg C
    Subcooled liquid VP: 7.56E-013 mm Hg (25 deg C, Mod-Grain method)
                       : 1.01E-010 Pa (25 deg C, Mod-Grain method)

 Water Solubility Estimate from Log Kow (WSKOW v1.41):
    Water Solubility at 25 deg C (mg/L):  4.609e-011
       log Kow used: 14.44 (estimated)
       no-melting pt equation used

 Water Sol Estimate from Fragments:
    Wat Sol (v1.01 est) =  6.3235e-007 mg/L

 ECOSAR Class Program (ECOSAR v1.00):
    Class(es) found:   Neutral Organics

 Henrys Law Constant (25 deg C) [HENRYWIN v3.20]:
   Bond Method :   Incomplete
   Group Method:   Incomplete
 For Henry LC Comparison Purposes:
   User-Entered Henry LC:  not entered
   Henrys LC [via VP/WSol estimate using User-Entered or Estimated values]:
      HLC:  4.892E-005 atm-m3/mole  (4.957E+000 Pa-m3/mole)
      VP:   2.71E-015 mm Hg (source: MPBPVP)
      WS:   4.61E-011 mg/L (source: WSKOWWIN)

 Log Octanol-Air Partition Coefficient (25 deg C) [KOAWIN v1.10]:
  Can Not Estimate (can not calculate HenryLC)

 Probability of Rapid Biodegradation (BIOWIN v4.10):
   Biowin1 (Linear Model)         :   0.6634
   Biowin2 (Non-Linear Model)     :   0.0925
 Expert Survey Biodegradation Results:
   Biowin3 (Ultimate Survey Model):   2.3984  (weeks-months)
```

```
  Biowin4 (Primary Survey Model) :   3.4736  (days-weeks  )
 MITI Biodegradation Probability:
  Biowin5 (MITI Linear Model)    :   0.4130
  Biowin6 (MITI Non-Linear Model):   0.1249
 Anaerobic Biodegradation Probability:
  Biowin7 (Anaerobic Linear Model):  0.8732
 Ready Biodegradability Prediction:   NO

Hydrocarbon Biodegradation (BioHCwin v1.01):
   Structure incompatible with current estimation method!

 Sorption to aerosols (25 Dec C)[AEROWIN v1.00]:
  Vapor pressure (liquid/subcooled):  1.01E-010 Pa (7.56E-013 mm Hg)
  Log Koa (): not available
  Kp (particle/gas partition coef. (m3/ug)):
      Mackay model           :  2.98E+004
      Octanol/air (Koa) model:  not available
  Fraction sorbed to airborne particulates (phi):
      Junge-Pankow model     :  1
      Mackay model           :  1
      Octanol/air (Koa) model:  not available

 Atmospheric Oxidation (25 deg C) [AopWin v1.92]:
  Hydroxyl Radicals Reaction:
     OVERALL OH Rate Constant =  42.9098 E-12 cm3/molecule-sec
     Half-Life =     0.249 Days (12-hr day; 1.5E6 OH/cm3)
     Half-Life =     2.991 Hrs
  Ozone Reaction:
     No Ozone Reaction Estimation
  Fraction sorbed to airborne particulates (phi):
     1 (Junge-Pankow, Mackay avg)
     not available (Koa method)
   Note: the sorbed fraction may be resistant to atmospheric oxidation

 Soil Adsorption Coefficient (KOCWIN v2.00):
     Koc    :  8.35E+007  L/kg (MCI method)
     Log Koc:  7.922       (MCI method)
     Koc    :  2.843E+008  L/kg (Kow method)
     Log Koc:  8.454       (Kow method)

 Aqueous Base/Acid-Catalyzed Hydrolysis (25 deg C) [HYDROWIN v2.00]:
   Rate constants can NOT be estimated for this structure!

 Bioaccumulation Estimates (BCFBAF v3.00):
  Log BCF from regression-based method = 0.500 (BCF = 3.162 L/kg wet-wt)
  Log Biotransformation Half-life (HL) = 2.6112 days (HL = 408.5 days)
  Log BCF Arnot-Gobas method (upper trophic) = -0.048 (BCF = 0.8945)
  Log BAF Arnot-Gobas method (upper trophic) = 0.850 (BAF = 7.079)
      log Kow used: 14.44 (estimated)

 Volatilization from Water:
   Henry LC:  4.89E-005 atm-m3/mole  (calculated from VP/WS)
   Half-Life from Model River:      32.66  hours   (1.361 days)
   Half-Life from Model Lake :      567.2  hours   (23.63 days)

 Removal In Wastewater Treatment:
   Total removal:              94.04  percent
```

```
   Total biodegradation:        0.78  percent
   Total sludge adsorption:    93.26  percent
   Total to Air:               0.00  percent
     (using 10000 hr Bio P,A,S)

 Removal In Wastewater Treatment (recommended maximum 95%):
   Total removal:              99.07  percent
   Total biodegradation:       37.17  percent
   Total sludge adsorption:    61.89  percent
   Total to Air:               0.00  percent
     (using Biowin/EPA draft method)

 Level III Fugacity Model:
         Mass Amount    Half-Life    Emissions
          (percent)        (hr)       (kg/hr)
   Air       0.177           5.98         1000
   Water     15.9            900          1000
   Soil      83.9          1.8e+003      1000
   Sediment  0.00575        8.1e+003      0
    Persistence Time: 1.21e+003 hr
```

ECOSAR Results for Magnesium Stearate:

```
SMILES : [Mg](OC(=O)CCCCCCCCCCCCCCCCC)OC(=O)CCCCCCCCCCCCCCCCC
CHEM   : Octadecanoic acid, magnesium salt
CAS Num: 000557-04-0
ChemID1:
ChemID2:
ChemID3:
MOL FOR: C36 H70 O4 Mg1
MOL WT : 591.26
Log Kow: 14.34  (KowWin estimate)
Melt Pt:
Wat Sol: 1.045E-010 mg/L  (WskowWin estimate)

ECOSAR v1.00 Class(es) Found
------------------------------
Neutral Organics
                                              Predicted
ECOSAR Class              Organism          Duration  End Pt   mg/L (ppm)
==========================  ==================  ========  ======   ==========
Neutral Organics         : Fish             96-hr     LC50    6.35e-009 *
Neutral Organics         : Fish             14-day    LC50    7.83e-009 *
Neutral Organics         : Daphnid            48-hr     LC50    2.22e-008 *
Neutral Organics         : Green Algae        96-hr     EC50    2.23e-006 *
Neutral Organics         : Fish             30-day    ChV     1.51e-009 *
Neutral Organics         : Daphnid                    ChV     1.82e-008 *
Neutral Organics         : Green Algae                 ChV     6.68e-006 *
Neutral Organics         : Fish  (SW)         96-hr     LC50    3.46e-009 *
Neutral Organics         : Mysid Shrimp        96-hr    LC50    9.53e-013
Neutral Organics         : Fish  (SW)                 ChV     1.11e-006 *
Neutral Organics         : Mysid Shrimp (SW)            ChV     2.13e-015
Neutral Organics         : Earthworm          14-day    LC50       54.019 *

 Note:  * = asterisk designates: Chemical may not be soluble
```

```
    enough to measure this predicted effect.

Neutral Organics:
----------------
  For Fish LC50 (96-h), Daphnid LC50, Mysid: If the log Kow is greater
than 5.0, or if the compound is solid and the LC50 exceeds the water
solubility by 10X, no effects at saturation are predicted.

  For Fish LC50 (14-day) and Earthworm LC50: If the log Kow is greater
than 6.0, or if the compound is solid and the LC50 exceeds the water
solubility by 10X, no effects at saturation are predicted.

  For Green Algae Acute Toxicity Values: If the log Kow of the chemical is
greater than 6.4, or if the compound is solid and the EC50 exceeds the water
solubility by 10X, no effects at saturation are predicted for these endpoints.

  For All Chronic Toxicity Values: If the log Kow of the chemical is greater
than 8.0, or if the compound is solid and the ChV exceeds the water solubility
by 10X, no effects at saturation are predicted for these endpoints.

ECOSAR v1.00 SAR Limitations:
---------------------------
Maximum LogKow: 5.0 (Fish 96-hr LC50; Daphnid LC50, Mysid LC50)
Maximum LogKow: 6.0 (Fish 14-day LC50; Earthworm LC50)
Maximum LogKow: 6.4 (Green Algae EC50)
Maximum LogKow: 8.0 (ChV)
Maximum Mol Wt: 1000
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```

Magnesium Stearate Green Screen Evaluation Prepared By:

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ToxServices LLC

Magnesium Stearate Green Screen Evaluation QC'd By:

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Margaret H. Whittaker, Ph.D., M.P.H., E.R.T., D.A.B.T.
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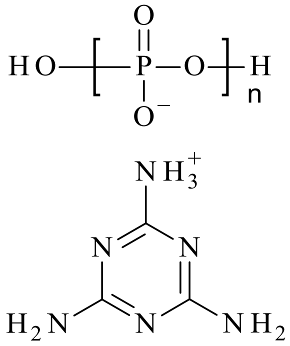
APPENDIX IX H: GREEN SCREEN FOR MELAMINE POLYPHOSPHATE (CAS #218768-84-4)[21]

Also Called: Polyphosphoric acids, compounds with melamine, Melapur 200

Chemical Structure of Melamine Polyphosphate:



***Note:** Data gaps for melamine polyphosphate (CAS #218768-84-4) were addressed using the structurally similar chemicals melamine phosphate (CAS #41583-09-9), melamine (CAS #108-78-1), and phosphate (CAS #14265-44-2) as surrogates.

For Polymers (Identify Monomers and Corresponding Properties):
% of Each Monomer – n/a
Are the monomers blocked? (Y/N) – n/a
Molecular Weight (MW) of Polymer >1,000 (U.S. EPA 2008b)
% of Polymer with – n/a
  a) MW <500
  b) MW <1,000
% Weight Residual Monomers – n/a
Solubility/Dispersability/Swellability – 20 g/L (U.S. EPA 2008b)
Particle Size – n/a
Overall Polymer Charge – n/a

Identify Applications/Functional Uses: Flame retardant.

Green Screen Rating[22]: Melamine polyphosphate was assigned a Benchmark Score of 2 based on High systemic toxicity (ST), and Moderate carcinogenicity (C) and mutagenicity (M) (2d).

Green Screen (Version 1) Levels of Concern for Melamine Polyphosphate														
Human – Tier 1					**Human – Tier 2**				**Eco**		**Fate**		**Physical**	
C	**M**	**R/D**	**ED**	**N**	**AT**	**Cr**	**Sn**	**ST**	**AA**	**CA**	**P**	**B**	**Ex**	**F**
M	*M*	L	nd	nd	L	L	*L*	*H*	*L*	*L*	*M*	L	L	L

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[21] CPA recommends independent third-party validation of all Green Screen assessments. No independent third-party validation has been done for this assessment . Companies may not make marketing claims based on a Green Screen assessment that has not undergone an independent validation.

[22] For inorganic chemicals with low human and ecotoxicity across all hazard endpoints and low bioaccumulation, persistence alone will not be deemed problematic. Inorganic chemicals that are only persistent will be evaluated under the criteria for Benchmark 4.

*Endpoints in italics were assigned using estimated values and professional judgment (Structure Activity Relationships).

Transformation Products and Ratings:
Identify relevant fate and transformation products (i.e., dissociation products, transformation products, valence states) and/or moieties of concern[23]

Life Cycle Stage	Transformation Pathway	Transformation Products	CAS #	Green Screen Rating
End of Life	Combustion; Biodegradation	Melamine	108-78-1	Not present on Red List of Chemicals (CPA 2009)
End of Life	Combustion; Biodegradation	Phosphate ion	14265-44-2	Not present on Red List of Chemicals (CPA 2009)
End of Life	Combustion	Melamine pyrophosphate	15541-60-3	Not present on Red List of Chemicals (CPA 2009)
End of Life	Combustion	Phosphoric acid	7664-38-2	Not present on Red List of Chemicals (CPA 2009)
End of Life	Combustion	Hydrogen cyanide	74-90-8	Potential neurotoxicant (CPA 2009)
End of Life	Combustion	Melamine polyphosphates	20208-95-1	Not present on Red List of Chemicals (CPA 2009)

*The above transformation products were screened against the CPA's table of Red List chemicals.

Introduction

Melamine phosphates are salts of melamine and phosphoric acid. These salts have good properties of thermal stability and are commonly used as flame retardants (UNEP 1997). Melamine and its derivatives (cyanurate, phosphates) are currently used in flexible polyurethane foams, intumescent coatings, polyamides and thermoplastic polyurethanes. There were not extensive data for melamine polyphosphate. In cases of data gaps, data for melamine phosphate, and the ions for melamine and phosphate were considered.

The U.S Food and Drug Administration (U.S. FDA) established a TDI (Tolerable Daily Intake) for melamine of 0.63 mg/kg bw/day (U.S. FDA 2007). This TDI was based on the results of a 13-week rat study of melamine (see reproductive toxicity section) and incorporates safety factors totaling 100. There is recent, strong evidence to suggest that the toxicity of melamine and cyanurate is synergistic (see repeat dose toxicity section). Based on these relatively new data, the U.S. FDA applied an additional 10-fold safety

---

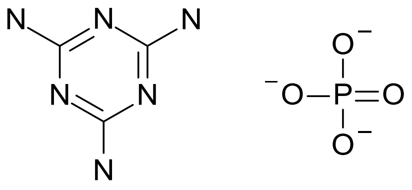
[23] A moiety is a discrete chemical entity that is a constituent part or component of a substance. A moiety of concern is often the parent substance itself for organic compounds. For inorganic compounds, the moiety of concern is typically a dissociated component of the substance or a transformation product.

factor to yield a combined safety factor of 1000-fold. Therefore, a TDI of 0.063 mg/kg bw/day was proposed (U.S. FDA 2008).

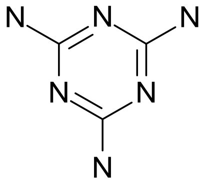
Melamine is degraded by three successive deamination reactions to ammeline (4,6-diamino-2-hydroxy-1,3,5-triazine), ammelide (6-amino-2,4- dihydroxy-1,3,5-triazine) and cyanuric acid(s- triazine-2,4,6-triol).

Melamine and phosphate are the expected breakdown products of melamine phosphate in the environment. The following chemical screen primarily uses toxicity data on melamine when the database for melamine phosphate is absent. Phosphate ion is also evaluated with regard to environmental parameters, but is not included in the human health analysis, as it is not expected to pose a risk to humans (U.S. EPA 1993).

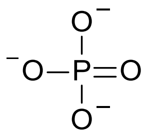
Chemical Structure of Surrogate:



Melamine phosphate (CAS #41583-09-9)



Melamine (CAS #108-78-1)



Phosphate (CAS #14265-44-2)

Human Health – Tier 1

Carcinogenicity (C) Score (H, M or L): *M*

Because no relevant carcinogenicity data for melamine polyphosphate were identified, the structurally similar melamine was used as a surrogate. Melamine polyphosphate was assigned a score of Moderate for carcinogenicity due to the conflicting evidence of carcinogenic properties for the surrogate, melamine, which induced bladder carcinomas in several animal studies.

***Note**: Unless specifically noted, information regarding animal strain or sex, dose, route of exposure, duration of experiment, or if these studies followed GLP guidelines was not provided by the authors of these studies.

Melamine polyphosphate

- Melamine polyphosphate is not listed as a known carcinogen by IARC, NTP, U.S. EPA, or CA Prop 65.

Melamine

- Significant formation of transitional cell carcinomas in the urinary bladder of male rats and significant chronic inflammation in the kidney of dosed female rats were observed. Carcinoma formation was significantly correlated with the incidence of bladder stones. A transitional-cell papilloma was observed in the urinary bladder of a single high dose male rat, and compound related lesions were observed in the urinary tract of dosed animals. Based on the mechanical nature of tumor formation, FDA and EPA considered melamine noncarcinogenic (U.S. EPA 2008).
- Increased incidence of acute and chronic inflammation and epithelial hyperplasia of the urinary bladder was observed in male mice. Bladder stones and compound related lesions were observed in the urinary tract of test animals. Melamine was not considered carcinogenic. No information concerning dose, route of administration, or other study details were provided (U.S. EPA 2008).
- Melamine-induced proliferative lesions of the rat urinary tract were directly due to the irritative stimulation of calculi, and not to molecular interactions between melamine or its metabolites with the bladder epithelium (U.S. EPA 2008).
- Water intake, used as an index of urinary output, was increased by NaCl treatment. Calculus formation resulting from melamine administration was suppressed dose-dependently by the simultaneous NaCl treatment. The main constituents of calculi were melamine and uric acid (total contents 61.1– 81.2%). The results indicate that melamine-induced proliferative lesions of the urinary tract of rats were directly due to the irritative stimulation of calculi, and not molecular interactions between melamine itself or its metabolites with the bladder epithelium (U.S. EPA 2008).
- As an initiator, melamine caused no significant increase in papillomas per mouse when compared to controls (U.S. EPA 2008).
- Diffuse papillary hyperplasia of the bladder epithelium and bladder calculi were observed in all melamine treated rats. Elevated spermidine/spermine N1-acetyltransferase (SAT) activity following melamine treatment was considered to be an indicator of cell proliferation (U.S. EPA 2008).
- Bladder tumors were only observed in the male rat and not in female rats or mice of either sex. An experiment did not reveal melamine as a tumor initiator. The formation of bladder stones and subsequent irritation of the bladder epithelium are necessary for tumor induction. Melamine is only indirectly responsible for the occurrence of bladder tumors. The incidence of calculi is dose dependent. The mechanism for tumor production is a non-genotoxic one. A threshold of 126 mg/kg for the formation of neoplasms can therefore be established. This value is based on a 2-year NTP feeding study with male Fisher 344 rats. The toxicity potential of melamine itself is considered low by the Consumer Product Safety Commission (Thomas and Brundage 2004).

Mutagenicity (M) and Genotoxicity Score (H, M or L): *M*

Because no relevant mutagenicity or genotoxicity data for melamine polyphosphate were identified, the structurally similar melamine was used as a surrogate. Melamine polyphosphate was assigned a score of Moderate for mutagenicity and genotoxicity due to the conflicting evidence of genotoxic properties for the surrogate, melamine, which induced chromosomal damage in several animal studies.

***Note**: Unless specifically noted, information regarding animal strain or sex, dose, route of exposure, duration of experiment, or if these studies followed GLP guidelines was not provided by the authors of these studies.

<u>Melamine</u>

- Bacterial forward mutation assay: Negative with and without liver activation (U.S. EPA 2008).
- *In vitro* mouse lymphoma test: Negative with and without liver activation (U.S. EPA 2008).
- *In vivo* mouse micronucleus test: The initial test gave a positive trend (P=0.003) for chromosomal damage; however, both peripheral blood smears and the repeat bone marrow test were negative. The overall conclusion was that melamine does not induce chromosomal damage (U.S. EPA 2008).
- *In vitro* chromosomal aberrations test: Negative in Chinese hamster ovary cells (CHO) with and without liver activation (U.S. EPA 2008).
- *In vitro* sister chromatid exchange assay: Negative in Chinese hamster ovary cells (CHO) with and without liver activation (U.S. EPA 2008).
- *In vivo* chromosome aberrations test in mice: Positive (U.S. EPA 2008).
- *In vivo* sister chromatid exchange assay in mice: Positive (U.S. EPA 2008)
- SOS/*umu* test: Negative for its ability to result in DNA damage and induce the expression of the *umu* operon (U.S. EPA 2008)
- Sex-linked recessive lethal/reciprocal translocation: Results were considered equivocal based on 0.18% and 0.36% total lethals following oral and injection exposure, respectively, compared to control total lethals of 0.07% for oral and 0.09% for injection (U.S. EPA 2008).
- *In vitro* flow cytometric (FCM) DNA repair assay: Negative for genotoxic effects (U.S. EPA 2008).
- Microscreen assay: Positive for genetic toxicity in *E. coli* WP2 uvrA assay (U.S. EPA 2008).

Reproductive (R) and Developmental (D) Toxicity Score (H, M or L): *L*

Because no relevant reproductive or developmental toxicity data were identified for melamine polyphosphate, the structurally similar melamine was used as a surrogate. Melamine polyphosphate was assigned a score of Low for reproductive and developmental toxicity because no basis of concern was identified.

***Note**: Unless specifically noted, information regarding animal strain or sex, dose, route of exposure, duration of experiment, or if these studies followed GLP guidelines was not provided by the authors of these studies.

<u>Melamine</u>

- Reproductive dysfunction was observed at 0.5 mg/m^3 and included effects on spermatogenesis (genetic material, sperm morphology, motility, and count), effects on the embryo/fetus (fetal death), preimplantation mortality (reduction in the number of implants per female), and total number of implants per corpora lutea (U.S EPA 2008).
- Mammary glands, ovaries, prostate, seminal vesicles, testes and uterus were examined macroscopically and microscopically in 13-week and in chronic toxicity studies with rats and mice and were found to be unaffected by melamine at each of the doses used. The lowest NOEL for systemic toxicity in these studies was 63 mg/kg/day (UNEP 1998).
- Melamine was not teratogenic in an investigation with rats. The NOEL for the fetuses was 1060 mg/kg/day, the highest dose tested. A maternal NOEL of 400 mg/kg/day was established based on decreased body weight and feed consumption and hematuria (UNEP 1998).

Endocrine Disruption (ED) Score (H, M or L): nd

- Melamine polyphosphate is not listed as a potential endocrine disruptor on the EU Priority List of Suspected Endocrine Disruptors.
- Melamine polyphosphate is not listed as a potential endocrine disruptor on the OSPAR List of Chemicals of Possible Concern.
- Melamine polyphosphate is not listed as a potential endocrine disruptor on the Red List of Chemicals (CPA 2009).

Neurotoxicity (N) Score (H, M or L): nd

- Melamine polyphosphate is not classified as a developmental neurotoxicant (Grandjean and Landrigan 2006).
- Melamine polyphosphate is not listed as a potential neurotoxicant on the Red List of Chemicals (CPA 2009).

Human Health – Tier 2

Acute Mammalian (AT) Toxicity Score (H, M or L): L

Melamine polyphosphate was assigned a score of Low for acute mammalian toxicity based on oral and dermal LD_{50} values of 2,000 or less mg/kg-bw from analog data. Data is from three different chemicals using two different routes of exposure in three different species of animals.

Melamine polyphosphate

- *Oral*: An LD_{50} of > 2,000 mg/kg was determined in the rat (U.S. EPA 2008).

Melamine phosphate

- *Oral*: An LD_{50} of > 2,000 mg/kg was determined in the mouse (Ciba 2005).
- *Dermal*: An LD_{50} of > 2,000 mg/kg was determined in the rabbit (Hummel Croton 2009).

Melamine

- *Oral*: An LD_{50} of 3,161 mg/kg (male) and 3,828 mg/kg (female) was determined in the rat (U.S. EPA 2008).
- *Oral*: An LD_{50} of > 6,400 mg/kg-bw was determined in the rat (U.S. EPA 2008).
- *Oral*: An LD_{50} of 3,296 mg/kg (male) and 7,014 mg/kg (female) was determined in the mouse (U.S. EPA 2008).
- *Oral*: An LD_{50} of 4,550 mg/kg was determined in the mouse (U.S. EPA 2008).
- *Dermal*: An LD_{50} of > 1,000 mg/kg was determined in the rabbit (U.S. EPA 2008).

Corrosion/ Irritation (Skin/ Eye) (Cr) Score (H, M or L): L
Melamine polyphosphate was assigned a score of Low for corrosion and irritation because no cause for concern was identified.

Melamine polyphosphate

- *Dermal*: Melamine polyphosphate was not irritating (no other data provided) (U.S. EPA 2008).
- *Ocular*: Melamine polyphosphate was slightly irritating (no other data provided) (U.S. EPA 2008).

Sensitization (Sn) Score (Skin and Respiratory) (H, M or L): *L*
Because no relevant sensitization data for melamine polyphosphate were identified, the structurally similar melamine phosphate and melamine were used as surrogates. Melamine polyphosphate was assigned a score of Low for sensitization because no basis for concern was identified.

Melamine Phosphate

- Melamine phosphate was not sensitizing in guinea pigs under Test Method OECD 406 (Ciba 2005).

Melamine

- Melamine was not sensitizing in human or guinea pig repeat insult patch test (UNEP 1998).

Systemic/ Organ (ST) Toxicity Score (includes organ effects and immunotoxicity) (H, M or L): *H*
Because no relevant systemic/organ toxicity data for melamine polyphosphate were identified, the structurally similar melamine was used as a surrogate. Melamine polyphosphate was assigned a score of High for systemic/organ toxicity based on analog data suggesting melamine causes kidney and bladder toxicity in animals.
***Note**: Unless specifically noted, information regarding animal strain or sex, dose, route of exposure, duration of experiment, or if these studies followed GLP guidelines was not provided by the authors of these studies.

Melamine

- Clinical signs observed during a 28-day repeat-dose study in rats included a dose-related increase in pilo-erection, lethargy, bloody urine spots in the cage and on the pelage of animals, and chromodacryorrhea. The incidence of urinary bladder calculi and urinary bladder hyperplasia in treated animals was dose dependant, with a significant relationship between the calculi and hyperplasia. Calculi composition indicated the presence of an organic matrix containing melamine, phosphorus, sulfur, potassium, and chloride. Crystals of dimelamine monophosphate were identified in the urine. The NOAEL was estimated to be 2000 ppm (240 mg/kg/day), excluding the observed increase in water consumption and the incidence of crystalluria. The LOAEL was determined to be 4,000 ppm (475 mg/kg/day) based on the formation of calculus (U.S. EPA 2008).

- Following a 90-day repeat-dose study in rats, one male rat receiving 18000 ppm and two males receiving 6,000 ppm died. Mean body weight gain and feed consumption were reduced. Stones and diffuse epithelial hyperplasia in the urinary bladders were observed. Focal epithelial hyperplasia was observed in only 1 male. A second and third 13-week repeated dose toxicity study was conducted in rats at a dose range of 750 to 18000 ppm in order to determine the No Observed Adverse Effect Level; however, bladder stones were observed at all dose levels. At 18000 ppm, stones occurred in diets with and without the addition of ammonium chloride (U.S. EPA 2008).
- A single female mouse died after receiving 9000 ppm in a 90-day repeat-dose study. Mean body weight gain relative to controls was depressed. The incidence of mice with bladder stones was dose-related and was greater in males than in females. Sixty percent of mice having bladder ulcers also had urinary bladder stones. Bladder ulcers were multifocal or associated with inflammation (cystitis). Epithelial hyperplasia and bladder stones were observed together in 2 mice. Also, epithelial cell atypia was seen. No observed adverse effects were noted at 6000 ppm (U.S. EPA 2008).
- Following the incidence of melamine contamination in pet food, a pilot study was carried out in which cats (one per dose) were fed melamine, cyanuric acid, or a combination of both. For the melamine only group, one cat was fed 0.5% (181 mg/kg/day) and one cat, 1% (44-121 mg/kg/day) of the chemical for 11 days. In the cyuranic acid only group, one cat was fed 0.2% (49 mg/kg/day) for 4 days, 0.5% (121 mg/kg/day) for 3 days, and then 1% (243 mg/kg/day) for 3 days. In the final group, one cat received 32 mg/kg of each compound, one cat received 121 mg/kg of each compound, and one cat received 181 mg/kg of each compound for one day. On the second day, cats ate nothing or very little. The estimated doses were 2 mg/kg, 10 mg/kg, or 54 mg/kg of each compound. Cats dosed with a combination experienced acute renal failure and had to be euthanized after 48 hours. Findings included amorphous, rounded and fan-shaped crystals in the urine, and histologic lesions in the kidneys, the severity of which corresponded to the dose[24]. No effect on any renal parameter was observed in cats fed melamine or cyanuric acid alone (Puschner 2007).
- 400 mg/kg of either melamine or cyanuric acid or melamine and cyanuric acid was fed daily for 3 days to 75 fish, 4 pigs, and 1 cat. Animals were euthanized 1, 3, 6, 10, or 14 days later. All animals fed the combination of melamine and cyanuric acid developed renal crystals arranged in radial spheres. Melamine and cyanuric acid residues were identified in edible tissues of fish (Reimschuessel 2008).

Ecotoxicity

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[24] The GHS category for toxic effects produced from a single exposure at ≤ 300 mg/kg/day or from multiple exposures at ≤ 2000 mg/kg/day is category 1.

Acute Aquatic (AA) Toxicity Score (H, M or L): *L*
Because no relevant acute aquatic toxicity data were identified for melamine polyphosphate and EPI Suite did not produce any results for ecotoxocity data, the structurally similar melamine phosphate, melamine, and phosphate were used as surrogates. Melamine polyphosphate was assigned a score of Low for acute aquatic toxicity based on L/EC$_{50}$ values of 100 mg/L or greater.

Melamine Phosphate

- An LC$_{50}$ of 100 mg/L was identified in a freshwater fish species (96 hour) (Ciba 2005).
- An EC$_{50}$ of > 100 mg/L was identified *Daphnia magna* (aquatic invertebrate, 48 hour) (Ciba 2005).

Melamine

- An LC$_{50}$ of > 500 mg/L was identified in *Leuciscus idus melanotus* (freshwater fish, 96 hour) (U.S. EPA 2008).
- An LC$_{50}$ of > 3,000 mg/L was identified in *Poecilia reticulate* (freshwater fish, 96 hour) (UNEP 1998).
- An LC$_{50}$ of > 2,000 mg/L was identified in *Daphnia magna* (aquatic invertebrate, 48 hour) (U.S. EPA 2008).
- An EC$_{50}$ of > 2,000 mg/L was identified in *Daphnia magna* (aquatic invertebrate, 48 hour) (UNEP 1998).
- An EC$_{50}$ of 940 mg/L was identified in *Scenedesmus pannonicus* (green algae, 96 hour) (U.S. EPA 2008).

Phosphate

- This chemical is designated to the ECOSAR class neutral organics. The most conservative estimated L/EC$_{50}$ acute values for fish (96-hr), daphnid (48-hr), and green algae (96-hr) are >100 mg/L (U.S. EPA 2009).

Chronic Aquatic (CA) Toxicity Score (H, M or L): *L*
Because no chronic aquatic toxicity data were identified for melamine polyphosphate and EPI Suite did not produce any results for ecotoxocity data, the structurally similar melamine and phosphate were used as surrogates. Melamine polyphosphate was assigned a score of Low for chronic aquatic toxicity based on NOEC values greater than 10 mg/L.

Melamine

- An NOEC of 1,000 mg/L was identified in *Jordanella floridae* (freshwater fish, 35 day) (U.S. EPA 2008).
- An NOEC of < 125 to > 1,000 mg/L was identified in a freshwater fish species (UNEP 1998).
- An LC$_{50}$ of 32-56 mg/L was identified in *Daphnia magna* (aquatic invertebrate, 21 day) (U.S. EPA 2008).
- An LC$_{50}$ of > 32 mg/L was identified in *Daphnia magna* (aquatic invertebrate, 21 day) (UNEP 1998).
- An NOEC of 18 mg/L was identified in *Daphnia magna* (aquatic invertebrate, 21 day) (UNEP 1998).

- An EC_{50} of 1,680 mg/L was identified in an aquatic plant species (14 day) (UNEP 1998).

Phosphate

- This chemical is designated to the ECOSAR class neutral organics. The most conservative estimated L/EC_{50} chronic values for fish (30-day), daphnid (duration not given), and green algae (duration not given) are >100 mg/L (U.S. EPA 2009).

Environmental Fate

Persistence (P) Score (vH, H, M, or L): *M*

Because no relevant persistence data for melamine polyphosphate were identified, the structurally similar melamine phosphate, melamine, and phosphate were used as surrogates. Melamine polyphosphate was assigned as score of Moderate for persistence based on analog data suggesting melamine polyphosphate will not biodegrade rapidly.

Melamine polyphosphate

- Based on evidence from melamine, melamine polyphosphate is expected to show moderate persistence and will not biodegrade rapidly (U.S. EPA 2008)

Melamine phosphate

- EPI Suite was unable to predict the environmental fate of melamine phosphate. Because it is a salt, it is expected to dissociate readily in the environment. Therefore, it is appropriate to evaluate the persistence of the two component ions instead.
- Above ~200°C melamine phosphate will react to melamine pyro-phosphate with release of reaction water, which will result in a heat sink. Above ~260°C melamine-pyrophosphate will react under release of reaction water to melamine-polyphosphates which again results in a heat sink effect. Above 350°C, melamine-polyphosphate undergoes endothermic decomposition and releases phosphoric acid (Ciba 2005).

Melamine

- A standard 5-day biochemical oxygen demand (BOD) test indicated melamine was not biodegradable (Saski 1970).
- Pure culture studies of *Pseudomonas* strain A exposed to 3mM melamine indicated that melamine is degraded to ammeline and eventually cyanuric acid (Jutzi 1982).
- Water is the most relevant compartment in the environmental fate of the substance (UNEP 1998).
- In water, melamine is expected to adsorb to sediment at acidic pHs (Weber 1970).
- Melamine is not expected to undergo hydrolysis in the environment due to the lack of functional groups that hydrolyze under environmental conditions (Lyman 1990).
- Melamine can be hydrolyzed by mineral acid or inorganic alkali (Crews 2005).

Phosphate

- The phosphate anion is expected to adsorb strongly to soil or colloidal particles in the water column. Salts of phosphoric acid generally dissociate (U.S EPA 1993).

Bioaccumulation (B) Score (vH, H, M, or L): L
Melamine polyphosphate was assigned a score of Low for bioaccumulation based on professional opinion and analog data that suggests the chemical will not bioaccumulate.

Melamine polyphosphate

- Because of its high water solubility (20g/L), the bioconcentration factor (BCF) is expected to be <1,000 (U.S. EPA 2008).

Melamine

- The bioaccumulation potential of melamine is low. No remarkable contribution of food from aquatic organisms to the uptake of melamine in humans is therefore expected (UNEP 1998).

Phosphate

- BCFBAF predicts a bioconcentration factor (BCF) of 3.16 for phosphate (U.S. EPA 2010)

Physical Properties

Explosivity (Ex) Hazard Rating (H, M or L): L
Melamine polyphosphate was assigned a score of Low for reactivity because no basis for concern was identified.

- Melamine polyphosphate is not explosive (U.S. EPA 2008).

Flammability (F) Hazard Rating (H, M or L): L
Melamine polyphosphate was assigned a score of Low for flammability because no basis for concern was identified.

- Melamine polyphosphate is not flammable (U.S. EPA 2008).

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EPI Suite Results for Melamine:

```
CAS Number: 108-78-1
SMILES : n(c(nc(n1)N)N)c1N
CHEM   : 1,3,5-Triazine-2,4,6-triamine
MOL FOR: C3 H6 N6
MOL WT : 126.12
------------------------------ EPI SUMMARY (v4.00) --------------------------
 Physical Property Inputs:
    Log Kow (octanol-water):   ------
    Boiling Point (deg C)  :   ------
    Melting Point (deg C)  :   ------
    Vapor Pressure (mm Hg) :   ------
    Water Solubility (mg/L):   ------
    Henry LC (atm-m3/mole) :   ------

 Log Octanol-Water Partition Coef (SRC):
    Log Kow (KOWWIN v1.67 estimate) =  -0.38
    Log Kow (Exper. database match) =  -1.37
       Exper. Ref:  HANSCH,C ET AL. (1995)

Boiling Pt, Melting Pt, Vapor Pressure Estimations (MPBPVP v1.43):
    Boiling Pt (deg C):  329.78  (Adapted Stein & Brown method)
    Melting Pt (deg C):  133.08  (Mean or Weighted MP)
    VP(mm Hg,25 deg C):  8.93E-008  (Modified Grain method)
    VP (Pa, 25 deg C) :  1.19E-005  (Modified Grain method)
    MP  (exp database):  345 dec deg C
    VP  (exp database):  3.59E-10 mm Hg (4.79E-008 Pa) at 20 deg C
    Subcooled liquid VP: 5.25E-007 mm Hg (20 deg C, exp database VP )
                       : 7E-005 Pa  (20 deg C, exp database VP )

 Water Solubility Estimate from Log Kow (WSKOW v1.41):
    Water Solubility at 25 deg C (mg/L):  1e+006
       log Kow used: -1.37 (expkow database)
       no-melting pt equation used
     Water Sol (Exper. database match) =  3230 mg/L (20 deg C)
        Exper. Ref:  YALKOWSKY,SH & HE,Y (2003)

 Water Sol Estimate from Fragments:
    Wat Sol (v1.01 est) =  1040.5 mg/L

 ECOSAR Class Program (ECOSAR v1.00):
    Class(es) found:
       Anilines (amino-meta)
       Triazines
       Melamines

 Henrys Law Constant (25 deg C) [HENRYWIN v3.20]:
   Bond Method :   1.89E-013  atm-m3/mole  (1.92E-008 Pa-m3/mole)
   Group Method:   Incomplete
   Exper Database: 1.84E-14  atm-m3/mole  (1.86E-009 Pa-m3/mole)
 For Henry LC Comparison Purposes:
   User-Entered Henry LC:  not entered
   Henrys LC [via VP/WSol estimate using User-Entered or Estimated values]:
      HLC:  1.482E-014 atm-m3/mole  (1.502E-009 Pa-m3/mole)
      VP:   8.93E-008 mm Hg (source: MPBPVP)
```

```
     WS:   1E+006 mg/L (source: WSKOWWIN)

 Log Octanol-Air Partition Coefficient (25 deg C) [KOAWIN v1.10]:
  Log Kow used:  -1.37  (exp database)
  Log Kaw used:  -12.124  (exp database)
     Log Koa (KOAWIN v1.10 estimate):  10.754
     Log Koa (experimental database):  None

 Probability of Rapid Biodegradation (BIOWIN v4.10):
   Biowin1 (Linear Model)         :  -0.0042
   Biowin2 (Non-Linear Model)     :   0.0000
 Expert Survey Biodegradation Results:
   Biowin3 (Ultimate Survey Model):   2.2697  (weeks-months)
   Biowin4 (Primary Survey Model) :   3.2831  (days-weeks  )
 MITI Biodegradation Probability:
   Biowin5 (MITI Linear Model)    :  -0.0193
   Biowin6 (MITI Non-Linear Model):   0.0000
 Anaerobic Biodegradation Probability:
   Biowin7 (Anaerobic Linear Model): -0.0756
 Ready Biodegradability Prediction:   NO

Hydrocarbon Biodegradation (BioHCwin v1.01):
    Structure incompatible with current estimation method!

 Sorption to aerosols (25 Dec C)[AEROWIN v1.00]:
  Vapor pressure (liquid/subcooled):  7E-005 Pa (5.25E-007 mm Hg)
  Log Koa (Koawin est  ): 10.754
   Kp (particle/gas partition coef. (m3/ug)):
       Mackay model           :  0.0429
       Octanol/air (Koa) model:  0.0139
   Fraction sorbed to airborne particulates (phi):
       Junge-Pankow model     :  0.608
       Mackay model           :  0.774
       Octanol/air (Koa) model:  0.527

 Atmospheric Oxidation (25 deg C) [AopWin v1.92]:
   Hydroxyl Radicals Reaction:
      OVERALL OH Rate Constant =   0.6596 E-12 cm3/molecule-sec
      Half-Life =    16.216 Days (12-hr day; 1.5E6 OH/cm3)
   Ozone Reaction:
      No Ozone Reaction Estimation
   Fraction sorbed to airborne particulates (phi):
      0.691 (Junge-Pankow, Mackay avg)
      0.527 (Koa method)
    Note: the sorbed fraction may be resistant to atmospheric oxidation

 Soil Adsorption Coefficient (KOCWIN v2.00):
      Koc    :  32.28  L/kg (MCI method)
      Log Koc:  1.509       (MCI method)
      Koc    :  1  L/kg (Kow method)
      Log Koc:  0.000       (Kow method)

 Aqueous Base/Acid-Catalyzed Hydrolysis (25 deg C) [HYDROWIN v2.00]:
    Rate constants can NOT be estimated for this structure!

 Bioaccumulation Estimates (BCFBAF v3.00):
   Log BCF from regression-based method = 0.500 (BCF = 3.162 L/kg wet-wt)
```

```
  Log Biotransformation Half-life (HL) = -3.1607 days (HL = 0.0006907 days)
  Log BCF Arnot-Gobas method (upper trophic) = -0.049 (BCF = 0.8938)
  Log BAF Arnot-Gobas method (upper trophic) = -0.049 (BAF = 0.8938)
     log Kow used: -1.37 (expkow database)

 Volatilization from Water:
   Henry LC:  1.84E-014 atm-m3/mole  (Henry experimental database)
   Half-Life from Model River: 3.573E+010  hours   (1.489E+009 days)
   Half-Life from Model Lake : 3.898E+011  hours   (1.624E+010 days)

 Removal In Wastewater Treatment:
   Total removal:               1.85  percent
   Total biodegradation:        0.09  percent
   Total sludge adsorption:     1.75  percent
   Total to Air:                0.00  percent
     (using 10000 hr Bio P,A,S)

 Removal In Wastewater Treatment:
   Total removal:              21.97  percent
   Total biodegradation:       20.53  percent
   Total sludge adsorption:     1.44  percent
   Total to Air:                0.00  percent
     (using Biowin/EPA draft method)

 Level III Fugacity Model:
         Mass Amount    Half-Life    Emissions
          (percent)        (hr)       (kg/hr)
   Air       3.41e-007      389          1000
   Water     25             900          1000
   Soil      74.9           1.8e+003     1000
   Sediment  0.086          8.1e+003     0
     Persistence Time: 1.37e+003 hr
```

ECOSAR Results for Melamine:

```
SMILES : n(c(nc(n1)N)N)c1N
CHEM   : 1,3,5-Triazine-2,4,6-triamine
CAS Num: 000108-78-1
ChemID1:
ChemID2:
ChemID3:
MOL FOR: C3 H6 N6
MOL WT : 126.12
Log Kow: -0.38  (KowWin estimate)
Melt Pt:
Wat Sol: 3230 mg/L  (experimental database)

ECOSAR v1.00 Class(es) Found
------------------------------
Anilines (amino-meta)
Triazines
Melamines
                                                          Predicted
ECOSAR Class               Organism           Duration  End Pt   mg/L (ppm)
=========================  ==================  ========  ======   ==========
Anilines (amino-meta)      : Fish              96-hr     LC50     1863.183
```

```
Anilines (amino-meta)     : Daphnid          48-hr    LC50       6.837
Anilines (amino-meta)     : Green Algae      96-hr    EC50       2.789
Anilines (amino-meta)     : Fish                      ChV      186.204 !
Anilines (amino-meta)     : Daphnid                   ChV        0.069
Anilines (amino-meta)     : Green Algae               ChV        0.054 !

Triazines            : Fish             96-hr    LC50    42792.074 *
Triazines            : Daphnid          48-hr    LC50     4418.740 *
Triazines            : Green Algae      96-hr    EC50      276.519
Triazines            : Fish                      ChV      1007.473 !
Triazines            : Daphnid          21-day   ChV       150.580
Triazines            : Green Algae               ChV        39.539

Melamines            : Fish             96-hr    LC50      390.882
Melamines            : Daphnid          48-hr    LC50      274.094
Melamines            : Green Algae      96-hr    EC50      324.968
Melamines            : Fish                      ChV      1102.529
Melamines            : Daphnid                   ChV        16.591 !
Melamines            : Green Algae               ChV        81.248 !
========================== ================== ======== ====== ==========
Neutral Organic SAR       : Fish             96-hr    LC50   10068.581 *
(Baseline Toxicity)       : Daphnid          48-hr    LC50    4356.359 *
                          : Green Algae      96-hr    EC50     706.784
                          : Fish                      ChV     1007.473
                          : Daphnid                   ChV      264.059
                          : Green Algae               ChV      165.581
 Note:  * = asterisk designates: Chemical may not be soluble enough to measure this predicted effect.

 Note:  ! = exclamation designates: The toxicity value was determined from
    a predicted SAR using established acute-to-chronic ratios and ECOSAR
    regression techniques which are documented in the supporting Technical
    Reference Manual. When possible, this toxicity value should be
    considered in a weight of evidence approach.

Anilines (amino-meta):
---------------------
  For Fish and Daphnid Acute Toxicity Values: If the log Kow of the chemical
is greater than 5.0, or if the compound is solid and the LC50 exceeds the
water solubility by 10X, no effects at saturation are predicted for these
endpoints.

  For Green Algae Acute Toxicity Values: If the log Kow of the chemical is
greater than 6.4, or if the compound is solid and the EC50 exceeds the water
solubility by 10X, no effects at saturation are predicted for these endpoints.

  For All Chronic Toxicity Values: If the log Kow of the chemical is greater
than 8.0, or if the compound is solid and the ChV exceeds the water solubility
by 10X, no effects at saturation are predicted for these endpoints.

ECOSAR v1.00 SAR Limitations:
---------------------------
Maximum LogKow: 5.0 (LC50)
Maximum LogKow: 6.4 (EC50)
Maximum LogKow: 8.0 (ChV)
Maximum Mol Wt: 1000
 Triazines:
---------
```

For Fish and Daphnid Acute Toxicity Values: If the log Kow of the chemical is greater than 5.0, or if the compound is solid and the LC50 exceeds the water solubility by 10X, no effects at saturation are predicted for these endpoints.

For Green Algae Acute Toxicity Values: If the log Kow of the chemical is greater than 6.4, or if the compound is solid and the EC50 exceeds the water solubility by 10X, no effects at saturation are predicted for these endpoints.

For All Chronic Toxicity Values: If the log Kow of the chemical is greater than 8.0, or if the compound is solid and the ChV exceeds the water solubility by 10X, no effects at saturation are predicted for these endpoints.

ECOSAR v1.00 SAR Limitations:

Maximum LogKow: 5.0 (LC50)
Maximum LogKow: 6.4 (EC50)
Maximum LogKow: 8.0 (ChV)
Maximum Mol Wt: 1000

Melamines :

For Fish and Daphnid Acute Toxicity Values: If the log Kow of the chemical is greater than 5.0, or if the compound is solid and the LC50 exceeds the water solubility by 10X, no effects at saturation are predicted for these endpoints.

For Green Algae Acute Toxicity Values: If the log Kow of the chemical is greater than 6.4, or if the compound is solid and the EC50 exceeds the water solubility by 10X, no effects at saturation are predicted for these endpoints.

For All Chronic Toxicity Values: If the log Kow of the chemical is greater than 8.0, or if the compound is solid and the ChV exceeds the water solubility by 10X, no effects at saturation are predicted for these endpoints.

ECOSAR v1.00 SAR Limitations:

Maximum LogKow: 5.0 (LC50)
Maximum LogKow: 6.4 (EC50)
Maximum LogKow: 8.0 (ChV)
Maximum Mol Wt: 1000

Baseline Toxicity SAR Limitations:

Maximum LogKow: 5.0 (Fish 96-hr LC50; Daphnid LC50)
Maximum LogKow: 6.4 (Green Algae EC50)
Maximum LogKow: 8.0 (ChV)
Maximum Mol Wt: 1000

EPI Suite Results for Phosphate:

CAS Number: 14265-44-2
SMILES : OP(=O)(O)O
CHEM : PHOSPHATE
MOL FOR: H3 O4 P1

```
MOL WT : 98.00
------------------------------ EPI SUMMARY (v4.00) --------------------------
 Physical Property Inputs:
    Log Kow (octanol-water):   ------
    Boiling Point (deg C)  :   ------
    Melting Point (deg C)  :   ------
    Vapor Pressure (mm Hg) :   ------
    Water Solubility (mg/L):   ------
    Henry LC (atm-m3/mole) :   ------

 Log Octanol-Water Partition Coef (SRC):
    *** WARNING: Inorganic Compound (Outside Estimation Domain)
    Log Kow (KOWWIN v1.67 estimate) =  -0.77

Boiling Pt, Melting Pt, Vapor Pressure Estimations (MPBPVP v1.43):
   *** WARNING: Inorganic Compound (Outside Estimate Domain) ***
   *** WARNING: Estimations NOT VALID ***
    Boiling Pt (deg C):  480.00  (Adapted Stein & Brown method)
    Melting Pt (deg C):  90.27  (Mean or Weighted MP)
    VP(mm Hg,25 deg C):  6.09E-011  (Modified Grain method)
    VP (Pa, 25 deg C) :  8.12E-009  (Modified Grain method)
    MP  (exp database):  42.35 deg C
    Subcooled liquid VP: 8.76E-011 mm Hg (25 deg C, Mod-Grain method)
                       : 1.17E-008 Pa (25 deg C, Mod-Grain method)

 Water Solubility Estimate from Log Kow (WSKOW v1.41):
    *** WARNING: Inorganic Compound (Outside Estimation Domain)**
    Water Solubility at 25 deg C (mg/L):  5.386e+005
       log Kow used: -0.77 (estimated)        no-melting pt equation used

 Water Sol Estimate from Fragments:
    *** WARNING: Inorganic Compound (Outside Estimation Domain)***
    *** WARNING: Wat Sol Estimation NOT Valid ***
    Wat Sol (v1.01 est) =  1e+006 mg/L

 ECOSAR Class Program (ECOSAR v1.00):
    Class(es) found:
       Neutral Organics

 Henrys Law Constant (25 deg C) [HENRYWIN v3.20]:
   *** WARNING: Inorganic Compound (Outside Estimation Domain) **
   *** WARNING: Estimation NOT VALID **
   Bond Method :   7.60E-015  atm-m3/mole  (7.70E-010 Pa-m3/mole)
   Group Method:   Incomplete
 For Henry LC Comparison Purposes:
   User-Entered Henry LC:  not entered
   Henrys LC [via VP/WSol estimate using User-Entered or Estimated values]:
      HLC:  1.458E-017 atm-m3/mole  (1.477E-012 Pa-m3/mole)
      VP:   6.09E-011 mm Hg (source: MPBPVP)
      WS:   5.39E+005 mg/L (source: WSKOWWIN)

 Log Octanol-Air Partition Coefficient (25 deg C) [KOAWIN v1.10]:
   *** WARNING: Inorganic Compound (Outside Estimation Domain)**
   *** WARNING: Estimation NOT VALID ***
  Log Kow used:  -0.77  (KowWin est)
  Log Kaw used:  -12.508  (HenryWin est)
      Log Koa (KOAWIN v1.10 estimate):  11.738
```

```
    Log Koa (experimental database):  None

 Probability of Rapid Biodegradation (BIOWIN v4.10):
   *** WARNING: Inorganic Compound (Outside Estimation Domain)**
   *** WARNING: Estimation NOT VALID ***
  Biowin1 (Linear Model)         :   0.7009
  Biowin2 (Non-Linear Model)     :   0.8344
 Expert Survey Biodegradation Results:
  Biowin3 (Ultimate Survey Model):   2.9826  (weeks       )
  Biowin4 (Primary Survey Model) :   3.7064  (days-weeks  )
 MITI Biodegradation Probability:
  Biowin5 (MITI Linear Model)    :   0.4206
  Biowin6 (MITI Non-Linear Model):   0.4247
 Anaerobic Biodegradation Probability:
  Biowin7 (Anaerobic Linear Model):  0.8361
 Ready Biodegradability Prediction:   NO

Hydrocarbon Biodegradation (BioHCwin v1.01):
   Structure incompatible with current estimation method!

 Sorption to aerosols (25 Dec C)[AEROWIN v1.00]:
  Vapor pressure (liquid/subcooled):  1.17E-008 Pa (8.76E-011 mm Hg)
  Log Koa (Koawin est  ): 11.738
   Kp (particle/gas partition coef. (m3/ug)):
       Mackay model           :  257
       Octanol/air (Koa) model:  0.134
   Fraction sorbed to airborne particulates (phi):
       Junge-Pankow model     :  1
       Mackay model           :  1
       Octanol/air (Koa) model:  0.915

 Atmospheric Oxidation (25 deg C) [AopWin v1.92]:
   *** WARNING: Inorganic Compound (Outside Estimation Domain)***
  Hydroxyl Radicals Reaction:
    OVERALL OH Rate Constant =   0.4200 E-12 cm3/molecule-sec
    Half-Life =    25.467 Days (12-hr day; 1.5E6 OH/cm3)
  Ozone Reaction:
    No Ozone Reaction Estimation
  Fraction sorbed to airborne particulates (phi):
    1 (Junge-Pankow, Mackay avg)
    0.915 (Koa method)
   Note: the sorbed fraction may be resistant to atmospheric oxidation

 Soil Adsorption Coefficient (KOCWIN v2.00):
  *** WARNING: Inorganic Coumpound (Outside Estimation Domain) **
  *** WARNING: Estimation NOT VALID **
    Koc    :  1.407  L/kg (MCI method)
    Log Koc:  0.148       (MCI method)
    Koc    :  4.004  L/kg (Kow method)
    Log Koc:  0.603       (Kow method)

 Aqueous Base/Acid-Catalyzed Hydrolysis (25 deg C) [HYDROWIN v2.00]:
   Rate constants can NOT be estimated for this structure!

 Bioaccumulation Estimates (BCFBAF v3.00):
  Log BCF from regression-based method = 0.500 (BCF = 3.162 L/kg wet-wt)
  Log Biotransformation Half-life (HL) = -2.0250 days (HL = 0.009441 days)
```

```
  Log BCF Arnot-Gobas method (upper trophic) = -0.047 (BCF = 0.898)
  Log BAF Arnot-Gobas method (upper trophic) = -0.047 (BAF = 0.898)
      log Kow used: -0.77 (estimated)

 Volatilization from Water:
    Henry LC:  7.6E-015 atm-m3/mole  (estimated by Bond SAR Method)
    Half-Life from Model River: 7.626E+010  hours   (3.178E+009 days)
    Half-Life from Model Lake :  8.32E+011  hours   (3.466E+010 days)

 Removal In Wastewater Treatment:
    Total removal:              1.85  percent
    Total biodegradation:        0.09  percent
    Total sludge adsorption:     1.76  percent
    Total to Air:               0.00  percent
      (using 10000 hr Bio P,A,S)

 Removal In Wastewater Treatment:
    Total removal:             75.06  percent
    Total biodegradation:       74.44  percent
    Total sludge adsorption:     0.62  percent
    Total to Air:               0.00  percent
      (using Biowin/EPA draft method)

 Level III Fugacity Model:
         Mass Amount    Half-Life    Emissions
          (percent)        (hr)       (kg/hr)
   Air       0.000587        611          1000
   Water     37.3            360          1000
   Soil      62.7            720          1000
   Sediment  0.0704          3.24e+003    0
     Persistence Time: 591 hr
```

ECOSAR Results for Phosphate:

```
SMILES : OP(=O)(O)O
CHEM   : PHOSPHATE
CAS Num: 014265-44-2
ChemID1:
ChemID2:
ChemID3:
MOL FOR: H3 O4 P1
MOL WT : 98.00
Log Kow: -0.77  (KowWin estimate)
Melt Pt:
Wat Sol: 5.386E+005 mg/L  (WskowWin estimate)

ECOSAR v1.00 Class(es) Found
------------------------------
Neutral Organics
                                                  Predicted
ECOSAR Class              Organism          Duration  End Pt   mg/L (ppm)
==========================  ==================  ========  ======   ==========
Neutral Organics         : Fish             96-hr     LC50    20670.012
Neutral Organics         : Fish             14-day    LC50    19987.178
Neutral Organics         : Daphnid            48-hr     LC50     7739.504
Neutral Organics         : Green Algae        96-hr     EC50     1103.342
```

```
Neutral Organics       : Fish            30-day   ChV     1788.696
Neutral Organics       : Daphnid                  ChV      578.554
Neutral Organics       : Green Algae              ChV      265.686
Neutral Organics       : Fish  (SW)        96-hr   LC50   35468.875
Neutral Organics       : Mysid Shrimp      96-hr   LC50   1.49e+005
Neutral Organics       : Fish  (SW)               ChV      612.736
Neutral Organics       : Mysid Shrimp (SW)        ChV    29203.973
Neutral Organics       : Earthworm        14-day  LC50     330.099

 Note:  * = asterisk designates: Chemical may not be soluble enough to measure this predicted effect.

Neutral Organics:
----------------
  For Fish LC50 (96-h), Daphnid LC50, Mysid: If the log Kow is greater
than 5.0, or if the compound is solid and the LC50 exceeds the water
solubility by 10X, no effects at saturation are predicted.

  For Fish LC50 (14-day) and Earthworm LC50: If the log Kow is greater
than 6.0, or if the compound is solid and the LC50 exceeds the water
solubility by 10X, no effects at saturation are predicted.

  For Green Algae Acute Toxicity Values: If the log Kow of the chemical is
greater than 6.4, or if the compound is solid and the EC50 exceeds the water
solubility by 10X, no effects at saturation are predicted for these endpoints.

  For All Chronic Toxicity Values: If the log Kow of the chemical is greater
than 8.0, or if the compound is solid and the ChV exceeds the water solubility
by 10X, no effects at saturation are predicted for these endpoints.

ECOSAR v1.00 SAR Limitations:
----------------------------
Maximum LogKow: 5.0 (Fish 96-hr LC50; Daphnid LC50, Mysid LC50)
Maximum LogKow: 6.0 (Fish 14-day LC50; Earthworm LC50)
Maximum LogKow: 6.4 (Green Algae EC50)
Maximum LogKow: 8.0 (ChV)
Maximum Mol Wt: 1000
 ---------------------------------------------------------------------------
```

Melamine Polyphosphate Green Screen Evaluation Prepared By:

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APPENDIX IX I: GREEN SCREEN FOR RED PHOSPHORUS (CAS #7723-14-0)[25]

Also Called: Amgard CPC, Amgard CPC 405, Black phosphorus, Bonide blue death rat killer, Caswell No. 663, Common sense cockroach and rat preparations, EINECS 231-768-7, EPA Pesticide Chemical Code 066502, Exolit 385, Exolit 405, Exolit LPKN, Exolit LPKN 275, Exolit RP 605, Exolit RP 650, Exolit RP 652, Exolit RP 654, Exolit VPK-n 361, FR-T 2 (element), Gelber phosphor, Gelber phosphor [German], HSDB 1169, Hishigado, Hishigado AP, Hishigado CP, Hishigado NP 10, Hishigado PL, Hostaflam RP 602, Hostaflam RP 614, Hostaflam RP 622, Hostaflam RP 654, Masteret 70450, NVE 140, Nova Sol R 20, Novaexcel 140, Novaexcel 150, Novaexcel F 5, Novaexcel ST 100, Novaexcel ST 140, Novaexcel ST 300, Novared 120UF, Novared 120UFA, Novared 120VFA, Novared 140, Novared 280, Novared C 120, Novared F 5, Phosphorus, Phosphorus (red), Phosphorus-31, Rat-Nip, Red phosphorus, UNII-27YLU75U4W, Violet phosphorus, White Phosphorus

Chemical Structure of Red Phosphorus:

P

For Inorganic Chemicals:

Define Form & Physiochemical Properties

13. Particle size (e.g. silica of respirable size) – unknown
14. Structure (e.g. amorphous vs. crystalline) – Crystalline (O'Neil 2001)
15. Mobility (e.g. Water solubility, volatility) – 2.4 mg/L at 15˚C; 4.1 mg/L at 25˚C (ESIS 2000)

Identify Applications/Functional Uses: Flame retardant

Green Screen Rating[26]: Red phosphorus was assigned a Green Screen Benchmark Score of 1 based on the High human acute toxicity (AT) and systemic toxicity (ST) as well as the High neurotoxicity (N), which is a priority effect (1d).

Green Screen (Version 1) Levels of Concern for Red Phosphorus														
Human – Tier 1					Human – Tier 2				Eco		Fate		Physical	
C	M	R/D	ED	N	AT	Cr	Sn	ST	AA	CA	P	B	Ex	F
L	L	L	nd	H	H	H	L	H	L	M	M	L	H	H

*Endpoints in italics were assigned using estimated values and professional judgment (Structure Activity Relationships).

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[25] CPA recommends independent third-party validation of all Green Screen assessments. No independent third-party validation has been done for this assessment . Companies may not make marketing claims based on a Green Screen assessment that has not undergone an independent validation.

[26] For inorganic chemicals with low human and ecotoxicity across all hazard endpoints and low bioaccumulation, persistence alone will not be deemed problematic. Inorganic chemicals that are only persistent will be evaluated under the criteria for Benchmark 4.

Transformation Products and Ratings:
Identify relevant fate and transformation products (i.e., dissociation products, transformation products, valence states) and/or moieties of concern[27]

Life Cycle Stage	Transformation Pathway	Transformation Products	CAS #	Green Screen Rating
	Possible product of phosphorus coming in direct contact with air and water.	Phosphine	7803-51-2	Present on the Red List of Chemicals as a possible neurotoxicant (CPA 2009).
End of Life	Combustion	Phosphorus acids	10294-56-1 and 13598-36-2	Not present on the Red List of Chemicals (CPA 2009).
End of Life	Combustion	Polyphosphoric acids	8017-16-1	Not present on the Red List of Chemicals (CPA 2009).
End of Life	Decomposition	Phosphorus oxides	Multiple	Not present on the Red List of Chemicals (CPA 2009).
	Reaction with Water	Hypophosphrous acid	6303-21-5	Not present on the Red List of Chemicals (CPA 2009).
	Reaction with Water	Phosphoric acid	7664-38-2	Not present on the Red List of Chemicals (CPA 2009).

*The above transformation products were screened against the CPA‘s table of Red List chemicals.

Introduction

Phosphorus exists in three main alloptropic forms: white (sometimes called yellow phosphorus), black, and red (O‘Neil 2001). Red phosphorus is a stable transformation form of the element phosphorus (Leisewitz 2000). Toxicity data for red phosphorus produced conflicting conclusions; not all studies stated specifically the allotrope of phosphorus being tested therefore the results varied widely. Red phosphorus is less toxic than the white allotrope however; most studies did not distinguish between the red and the white forms and only identified the compound as ―phosphorus.” In an effort to be conservative, all data, unless it specifically stated white phosphorus was used, was taken into consideration.

Red phosphorus is an additive flame retardant stabilized by wetting it with additives or by micro-encapsulation with phenol formaldehyde resins. Red phosphorus decomposes

---

[27] A moiety is a discrete chemical entity that is a constituent part or component of a substance. A moiety of concern is often the parent substance itself for organic compounds. For inorganic compounds, the moiety of concern is typically a dissociated component of the substance or a transformation product.

thermally above 400˚C. Its mode of action involves forming a rigid, glassy carbonized layer on the polymer that consists mainly of polyphosphoric acid, which prevents the re-supply of flammable material in the gas phase. The oxygen required for the formation of the polyphosphoric acid is derived preferentially from the matrix (polymer or other material). This makes red phosphorus a highly effective flame retardant in materials with high oxygen content such as cellulose or other oxygen-containing plastics. A synergist is required in oxygen-free materials such as polyolefins or polystyrene. Impurities found in red phosphorus mainly stem from white phosphorus which ignites in the presence of air (up to 200 mg/kg red phosphorus).

Red phosphorus does not dissolve easily in water (Leisewitz 2000). Risks of environmental contamination with red phosphorus as a result of its use as a flame retardant is low, while inertial and micro-encapsulated red phosphorus do not pose a hazard to the environment. Oral ingestion of free RP is unlikely due to its degradability in the environment. Fumes can lead to irritations of the skin and mucous membranes. Lack of oxygen can lead to the formation of white phosphorus, also called yellow phosphorus, which can ignite in the presence of air. The National Institute for Occupational Safety and Health (NIOSH) has assigned red phosphorus an exposure limit of 0.1 mg/m^3 (TWA) and an immediately dangerous to life or health value (IDLH) of 5 mg/m^3 (Avogadro 2000). OSHA assigned red phosphorus a Permissible Exposure Limit (PEL) of 0.1 mg/m^3 (Avogadro 2000).

Human Health – Tier 1

Carcinogenicity (C) Score: (H, M or L): L

Red phosphorus was assigned a score of Low for carcinogenicity because no basis for concern was identified.

- Red phosphorus is not listed as a known carcinogen by IARC, NTP, U.S. EPA, or CA Prop 65.

Mutagenicity (M) and Genotoxicity Score: (H, M or L): L

Red phosphorus was assigned a score of Low for mutagenicity and genotoxicity because data from animal studies suggests the chemical is not clastogenic.

- Female rats were exposed to red phosphorus/butyl rubber at 1,000 mg/m^3 over a 2 week period. It was concluded the test substance was a weak clastogen. No other details of the study were provided (U.S. EPA 2010b).

Reproductive (R) and Developmental (D) Toxicity Score: (H, M or L): L

Red phosphorus was assigned a score of Low for reproductive and developmental toxicity because no basis for concern was identified.

- There are no data to suggest that a single inhalation exposure to red phosphorus would cause developmental or reproductive toxicity (no other data provided) (U.S. EPA 2010b).

Endocrine Disruption (ED) Score: (H, M or L): nd

- Red phosphorus is not listed as a potential endocrine disruptor on the EU Priority List of Suspected Endocrine Disruptors.
- Red phosphorus is not listed as a potential endocrine disruptor on the OSPAR List of Chemicals of Possible Concern.
- Red phosphorus is not listed as a potential endocrine disruptor on the Red List of Chemicals (CPA 2009).

Neurotoxicity (N) Score: (H, M or L): H
Red phosphorus was assigned a score of High for neurotoxicity based on it being listed as a potential neurotoxicant.

- Red phosphorus is classified as a developmental neurotoxicant (Grandjean and Landrigan 2006).
- Red phosphorus is listed as a potential neurotoxicant on the Red List of Chemicals (CPA 2009).

Human Health – Tier 2

Acute Mammalian (AT) Toxicity Score: (H, M or L): H
Red phosphorus was assigned a score of High for acute mammalian toxicity based on oral LD_{50} values < 50 mg/kg-bw. Data is based on studies from two routes of exposure in four different species.
***Note:** Unless specifically noted, it is unclear if these LD_{50} values apply to the red phosphorus or the white (more toxic) phosphorus.

- *Oral*: An LD_{50} of 3.3 mg/kg was determined in the rat (Avogadro 2000).
- *Oral*: An LD_{50} of 11.5 mg/kg was determined in the rat (ChemCAS 2004).
- *Oral*: An LD_{50} of 4.8 mg/kg was determined in the mouse (Avogadro 2000).
- *Oral*: An LD_{50} of 11.5 mg/kg was determined in the mouse (ChemCAS 2004).
- *Oral*: An LD_{50} of 105 mg/kg was determined in the rabbit (ChemCAS 2004).
- *Oral*: An LD_{50} of > 15,000 mg/kg-bw was determined for red phosphorus in the rat (ESIS 2000).
- *Oral*: A dosage of 0.66 mg/kg-bw (red phosphorus) did not kill rabbits or guinea pigs, but did induce cirrhosis-like symptoms (Hayes 1991).
- *Inhalation*: An LC_{50} (1 hour exposure time) of 4.3 mg/L (red phosphorus) was determined in the rat (ESIS 2000).

Corrosion/ Irritation (Skin/ Eye) (Cr) Score: (H, M or L): H
Red phosphorus was assigned a score of High for corrosion and irritation based on animal studies that showed the chemical to cause injury to skin and eyes.

- *Dermal*: Prolonged or repeated contact may cause irritation and/or dermatitis (Avogadro 2000).
- *Dermal*: If contaminated with white phosphorus, contact may cause deep, slow healing burns (J.T. Baker 2008).
- *Ocular*: May cause corneal injury (Avogadro 2000).
- *Ocular*: If contaminated with white phosphorus, contact can cause severe irritation and burns (J.T. Baker 2008).

Sensitization (Sn) Score (Skin and Respiratory): (H, M or L): L
Red phosphorus was assigned a score of Low for sensitization because no basis for concern was identified.

- *Dermal*: Red phosphorus is not sensitizing to guinea pigs (ESIS 2000)

Systemic/ Organ (ST) Toxicity Score (includes organ effects and immunotoxicity) (H, M or L): H
Red phosphorus was assigned a score or High for systemic/organ toxicity based on evidence of adverse effects in humans.

- Red phosphorus targets the liver and kidneys (Avogadro 2000).
- Chronic exposure to red phosphorus can lead to necrosis of the jaw or ―phossy-jaw" (Avogadro 2000).
- Chronic exposure to red phosphorus can lead to blood disorders and cardiovascular effects (J.T. Baker 2008).
- Persons with pre-existing skin disorders or eye problems, jaw/tooth abnormalities, or impaired liver, kidney or respiratory function may be more susceptible to the effects of red phosphorus (J.T. Baker 2008).
- Mice and rats were exposed to the smoke produced by ignition of a red phosphorus pyrotechnic composition, 1 hr/day, 5 days/week, at two different dose levels (actual doses not provided by the authors), together with controls. The mice received 180 exposures, while the rats received 200 exposures. Guinea pigs also underwent 200 exposures at the lower concentration, but all animals exposed at the higher concentration died during or immediately after the first dose. Growth of the test groups of mice and rats was depressed during the exposure period. Organ specific toxicity appeared not to be present in rats and was generally confined to the respiratory tract of the mice and the guinea pigs. A significantly higher proportion of the test group mouse lung showed aggregates of macrophages containing granules than was present in the control group. Severe congestion was observed in practically all the lung from the decedent high-dose group guinea pigs (Marrs 1989).

Ecotoxicity

Acute Aquatic (AA) Toxicity Score: (H, M or L): L
Red phosphorus was assigned a score of Low for acute aquatic toxicity based on LC_{50} values greater than 100 mg/L.

- An LC_{50} of 2,609 mg/L was identified in fish (96 hour) (U.S. EPA 2009).
- An LC_{50} of 1,051 mg/L was identified in the daphnid (aquatic invertebrate, 48 hour) (U.S. EPA 2009).
- An EC_{50} of 186 mg/L was identified in green algae (aquatic plant, 96 hour) (U.S. EPA 2009).

Chronic Aquatic (CA) Toxicity Score: (H, M or L): M

Red phosphorus was assigned a score of Moderate for chronic aquatic toxicity based on the risk phrase of R52/53,

- Red phosphorus was assigned the following Risk Phrase: R52/53- Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment (ChemCAS 2004).
- A ChV of 233 mg/L was identified in fish (30 day) (U.S. EPA 2009).
- A ChV of 85 mg/L was identified in daphnid (U.S. EPA 2009).
- A ChV of 48 mg/L was identified in green algae (U.S. EPA 2009).

Environmental Fate

Persistence (P) Score: (vH, H, M, or L): M

Red phosphorus was assigned a score of Moderate for persistence based on a half-life in soil of 30 days and a half-life in water of 15 days.

- EPI Suite – BIOWIN model results indicate phosphorus readily biodegrades, and has a predicted degradation time of days to weeks. STP removal expected using BIOWIN/EPA Draft Method results indicate 96.32% total removal, with 50.88% due to biodegradation. Fugacity modeling predicts 1.86% partitioning to soil with a half-life of 30 days, and 42.3% partitioning to water with a half-life of 15 days (U.S. EPA 2010a).

Bioaccumulation (B) Score: (vH, H, M, or L): L

Red phosphorus was assigned a score of Low for bioaccumulation based on a BCF less than 500.

- BCFBAF predicts a bioconcentration factor (BCF) of 0.9181 and a log K_{ow} of -0.27 (U.S. EPA 2010a).

Physical Properties

Explosivity (Ex) Hazard Rating: (H, M or L): H

Red phosphorus was assigned a score of High for explosivity based on the risk phrase R16.

- Red phosphorus was assigned the following Risk Phrase: R16- Explosive when mixed with oxidizing substances (Avogadro 2000).
- Lack of oxygen can lead to the formation of white phosphorus which is explosive when in contact with air (Leisewitz 2000).

Flammability (F) Hazard Rating: (H, M or L): H

Red phosphorus was assigned a score of High for flammability based on the risk phrase R11.

- Red phosphorus was assigned the following Risk Phrase: R11- Highly flammable (Avogadro 2000, ChemCAS 2004, J.T. Baker 2008).

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EPI Suite Results: Red Phosphorus:

```
CAS Number: 7723-14-0
SMILES : P
CHEM   : PHOSPHORUS
MOL FOR: H3 P1
MOL WT : 34.00
------------------------------ EPI SUMMARY (v4.00) --------------------------
 Physical Property Inputs:
    Log Kow (octanol-water):   ------
    Boiling Point (deg C)  :   ------
    Melting Point (deg C)  :   ------
    Vapor Pressure (mm Hg) :   ------
    Water Solubility (mg/L):   ------
    Henry LC (atm-m3/mole) :   ------

 Log Octanol-Water Partition Coef (SRC):
    *** WARNING: Inorganic Compound (Outside Estimation Domain)
    Log Kow (KOWWIN v1.67 estimate) =  -0.27

Boiling Pt, Melting Pt, Vapor Pressure Estimations (MPBPVP v1.43):
   *** WARNING: Inorganic Compound (Outside Estimate Domain) ***
   *** WARNING: Estimations NOT VALID ***
    Boiling Pt (deg C):  468.18  (Adapted Stein & Brown method)
    Melting Pt (deg C):  162.02  (Mean or Weighted MP)
    VP(mm Hg,25 deg C):  2.33E+004  (Mean VP of Antoine & Grain methods)
    VP (Pa, 25 deg C) :  3.11E+006  (Mean VP of Antoine & Grain methods)
    MP  (exp database):  -133 deg C
    BP  (exp database):  -87.7 deg C
    VP  (exp database):  2.93E+04 mm Hg (3.91E+006 Pa) at 25 deg C

 Water Solubility Estimate from Log Kow (WSKOW v1.41):
    *** WARNING: Inorganic Compound (Outside Estimation Domain)**
    Water Solubility at 25 deg C (mg/L):  2.048e+005
       log Kow used: -0.27 (estimated)
       no-melting pt equation used
     Water Sol (Exper. database match) =  3.3 mg/L (15 deg C)
        Exper. Ref:  KIRK-OTHMER; on-line (2005)

 Water Sol Estimate from Fragments:
    *** WARNING: Inorganic Compound (Outside Estimation Domain)***
    *** WARNING: Wat Sol Estimation NOT Valid ***
    Wat Sol (v1.01 est) =  60349 mg/L

 ECOSAR Class Program (ECOSAR v1.00):
    Class(es) found:        Neutral Organics

 Henrys Law Constant (25 deg C) [HENRYWIN v3.20]:
   *** WARNING: Inorganic Compound (Outside Estimation Domain) **
   *** WARNING: Estimation NOT VALID **
   Bond Method :   2.44E-002  atm-m3/mole  (2.48E+003 Pa-m3/mole)
   Group Method:   Incomplete
 For Henry LC Comparison Purposes:
   User-Entered Henry LC:  not entered
   Henrys LC [via VP/WSol estimate using User-Entered or Estimated values]:
      HLC:  1.660E-004 atm-m3/mole  (1.682E+001 Pa-m3/mole)
```

```
    VP:   2.33E+004 mm Hg (source: MPBPVP)
    WS:   2.05E+005 mg/L (source: WSKOWWIN)

 Log Octanol-Air Partition Coefficient (25 deg C) [KOAWIN v1.10]:
   *** WARNING: Inorganic Compound (Outside Estimation Domain)**
   *** WARNING: Estimation NOT VALID ***
  Log Kow used:  -0.27  (KowWin est)
  Log Kaw used:  -0.001  (HenryWin est)
    Log Koa (KOAWIN v1.10 estimate):  -0.269
    Log Koa (experimental database):  None

 Probability of Rapid Biodegradation (BIOWIN v4.10):
    *** WARNING: Inorganic Compound (Outside Estimation Domain)**
    *** WARNING: Estimation NOT VALID ***
   Biowin1 (Linear Model)         :   0.7314
   Biowin2 (Non-Linear Model)     :   0.9259
 Expert Survey Biodegradation Results:
   Biowin3 (Ultimate Survey Model):   3.1240  (weeks       )
   Biowin4 (Primary Survey Model) :   3.7987  (days        )
 MITI Biodegradation Probability:
   Biowin5 (MITI Linear Model)    :   0.6110
   Biowin6 (MITI Non-Linear Model):   0.8241
 Anaerobic Biodegradation Probability:
   Biowin7 (Anaerobic Linear Model):  0.8361
 Ready Biodegradability Prediction:   YES

Hydrocarbon Biodegradation (BioHCwin v1.01):
    Structure incompatible with current estimation method!

 Sorption to aerosols (25 Dec C)[AEROWIN v1.00]:
  Vapor pressure (liquid/subcooled):  3.91E+006 Pa (2.93E+004 mm Hg)
  Log Koa (Koawin est  ): -0.269
   Kp (particle/gas partition coef. (m3/ug)):
       Mackay model           :  7.68E-013
       Octanol/air (Koa) model:  1.32E-013
   Fraction sorbed to airborne particulates (phi):
       Junge-Pankow model     :  2.77E-011
       Mackay model           :  6.14E-011
       Octanol/air (Koa) model:  1.06E-011

 Atmospheric Oxidation (25 deg C) [AopWin v1.92]:
    *** WARNING: Inorganic Compound (Outside Estimation Domain)***
   Hydroxyl Radicals Reaction:
      OVERALL OH Rate Constant =   0.0000 E-12 cm3/molecule-sec
      Half-Life =   -------
   Ozone Reaction:
      No Ozone Reaction Estimation
   Fraction sorbed to airborne particulates (phi):
      4.46E-011 (Junge-Pankow, Mackay avg)
      1.06E-011 (Koa method)
    Note: the sorbed fraction may be resistant to atmospheric oxidation

 Soil Adsorption Coefficient (KOCWIN v2.00):
   *** WARNING: Inorganic Coumpound (Outside Estimation Domain) **
   *** WARNING: Estimation NOT VALID **
      Koc    :  13.22  L/kg (MCI method)
      Log Koc:  1.121       (MCI method)
```

```
     Koc    :  0.5825  L/kg (Kow method)
     Log Koc:  -0.235      (Kow method)

 Aqueous Base/Acid-Catalyzed Hydrolysis (25 deg C) [HYDROWIN v2.00]:
   Rate constants can NOT be estimated for this structure!

 Bioaccumulation Estimates (BCFBAF v3.00):
  Log BCF from regression-based method = 0.500 (BCF = 3.162 L/kg wet-wt)
  Log Biotransformation Half-life (HL) = -1.7075 days (HL = 0.01961 days)
  Log BCF Arnot-Gobas method (upper trophic) = -0.037 (BCF = 0.9181)
  Log BAF Arnot-Gobas method (upper trophic) = -0.037 (BAF = 0.9181)
      log Kow used: -0.27 (estimated)

 Volatilization from Water:
   Henry LC:  0.0244 atm-m3/mole  (estimated by Bond SAR Method)
   Half-Life from Model River:      0.609  hours   (36.54 min)
   Half-Life from Model Lake :      55.54  hours   (2.314 days)

 Removal In Wastewater Treatment:
   Total removal:              90.47  percent
   Total biodegradation:        0.02  percent
   Total sludge adsorption:     0.39  percent
   Total to Air:               90.06  percent
     (using 10000 hr Bio P,A,S)

 Removal In Wastewater Treatment (recommended maximum 95%):
   Total removal:              96.32  percent
   Total biodegradation:       50.88  percent
   Total sludge adsorption:     0.27  percent
   Total to Air:               45.18  percent
     (using Biowin/EPA draft method)

 Level III Fugacity Model:
         Mass Amount    Half-Life    Emissions
          (percent)        (hr)       (kg/hr)
  Air        55.7          1e+005       1000
  Water      42.3            360        1000
  Soil       1.86            720        1000
  Sediment   0.101         3.24e+003    0
    Persistence Time: 146 hr
```

ECOSAR Results: Red Phosphorus:

```
SMILES : P
CHEM   : PHOSPHORUS
CAS Num: 007723-14-0
ChemID1:
ChemID2:
ChemID3:
MOL FOR: H3 P1
MOL WT : 34.00
Log Kow: -0.27  (KowWin estimate)
Melt Pt:
Wat Sol: 3.3 mg/L  (experimental database)

ECOSAR v1.00 Class(es) Found
```

```
------------------------------
Neutral Organics
                                             Predicted
ECOSAR Class              Organism          Duration  End Pt   mg/L (ppm)
=========================  ================= ======== ======   ==========
Neutral Organics         : Fish             96-hr     LC50     2609.779 *
Neutral Organics         : Fish             14-day    LC50     2543.939 *
Neutral Organics         : Daphnid            48-hr     LC50     1051.975 *
Neutral Organics         : Green Algae        96-hr     EC50      186.249 *
Neutral Organics         : Fish             30-day    ChV       233.517 *
Neutral Organics         : Daphnid                    ChV        85.106 *
Neutral Organics         : Green Algae                ChV        48.739 *
Neutral Organics         : Fish  (SW)         96-hr     LC50     4311.682 *
Neutral Organics         : Mysid Shrimp        96-hr     LC50    13151.021 *
Neutral Organics         : Fish  (SW)                 ChV       103.053 *
Neutral Organics         : Mysid Shrimp (SW)            ChV      2228.113 *
Neutral Organics         : Earthworm          14-day    LC50      101.661 *

 Note:  * = asterisk designates: Chemical may not be soluble
       enough to measure this predicted effect.

Neutral Organics:
----------------
  For Fish LC50 (96-h), Daphnid LC50, Mysid: If the log Kow is greater
than 5.0, or if the compound is solid and the LC50 exceeds the water
solubility by 10X, no effects at saturation are predicted.

  For Fish LC50 (14-day) and Earthworm LC50: If the log Kow is greater
than 6.0, or if the compound is solid and the LC50 exceeds the water
solubility by 10X, no effects at saturation are predicted.

  For Green Algae Acute Toxicity Values: If the log Kow of the chemical is
greater than 6.4, or if the compound is solid and the EC50 exceeds the water
solubility by 10X, no effects at saturation are predicted for these endpoints.

  For All Chronic Toxicity Values: If the log Kow of the chemical is greater
than 8.0, or if the compound is solid and the ChV exceeds the water solubility
by 10X, no effects at saturation are predicted for these endpoints.

ECOSAR v1.00 SAR Limitations:
---------------------------
Maximum LogKow: 5.0 (Fish 96-hr LC50; Daphnid LC50, Mysid LC50)
Maximum LogKow: 6.0 (Fish 14-day LC50; Earthworm LC50)
Maximum LogKow: 6.4 (Green Algae EC50)
Maximum LogKow: 8.0 (ChV)
Maximum Mol Wt: 1000

----------------------------------------------------------------------------
```

Red Phosphorus Green Screen Evaluation Prepared By:

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ToxServices LLC

Red Phosphorus Green Screen Evaluation QC'd By:

Margaret H. Whittaker

Margaret H. Whittaker, Ph.D., M.P.H., E.R.T., D.A.B.T.
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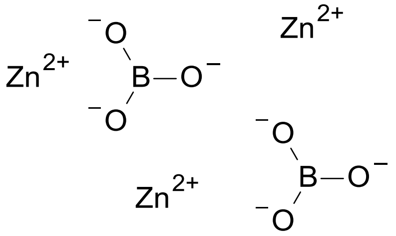
ToxServices LLC

APPENDIX IX J: GREEN SCREEN FOR ZINC BORATE (CAS #1332-07-6)[28]

Also Called: Alcanex FR 100, Alcanex FRC 600, Bonrex FC, Borax 2335, Boric acid, zinc salt, Climax ZB 467, EINECS 215-566-6, EPA Pesticide Chemical Code 128859, FRC 600, Flamtard Z 10, HSDB 1046, JS 9502, SZB 2335, XPI 187, ZB 112, ZB 237, ZB 467 Lite, ZN 100, ZSB 2335, ZT, ZT (fire retardant), Zinc borate

Chemical Structure of Zinc Borate:



***Note:** Data gaps for this chemical were addressed by evaluating the toxicity data on zinc oxide (CAS #1314-13-2) and boric acid (CAS #10043-35-3; 11113-50-1). ToxServices selected these chemicals as they are degradation products of the parent compound and structurally similar to the parent compound.

For Inorganic Chemicals:
Define Form & Physiochemical Properties

16. Particle size (e.g. silica of respirable size) – 8-20 □article size (e.g. silic
17. Structure (e.g. amorphous vs. crystalline) – n/a
18. Mobility (e.g. Water solubility, volatility) – 0.1% at pH 5 and 7, and 0.03% at pH 9 (U.S. EPA 1991)

Identify Applications/Functional Uses: Flame retardant.

Green Screen Rating[29]: Zinc borate was assigned a Benchmark Score of 2 based on a Moderate hazard rating for reproductive and developmental (R/D) toxicity (1d).

Green Screen (Version 1.0) Levels of Concern for Zinc Borate														
Human – Tier 1					**Human – Tier 2**				**Eco**		**Fate**		**Physical**	
C	**M**	**R/D**	**ED**	**N**	**AT**	**Cr**	**Sn**	**ST**	**AA**	**CA**	**P**	**B**	**Ex**	**F**
L	**L**	*M*	*M*	nd	**L**	**M**	**L**	**M**	**H**	nd	nd	**L**	**L**	**L**

*Endpoints in italics were assigned using estimated values and professional judgment (Structure Activity Relationships).

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[28] CPA recommends independent third-party validation of all Green Screen assessments. No independent third-party validation has been done for this assessment . Companies may not make marketing claims based on a Green Screen assessment that has not undergone an independent validation.

[29] For inorganic chemicals with low human and ecotoxicity across all hazard endpoints and low bioaccumulation, persistence alone will not be deemed problematic. Inorganic chemicals that are only persistent will be evaluated under the criteria for Benchmark 4.

Transformation Products and Ratings:
Identify relevant fate and transformation products (i.e., dissociation products, transformation products, valence states) and/or moieties of concern[30]

Life Cycle Stage	Transformation Pathway	Transformation Products	CAS #	Green Screen Rating
End of Life	Dissociation	Zinc, cation	23713-49-7	Not present on the Red List of Chemicals (CPA 2009)
End of Life	Dissociation	Borate, anion	39201-27-9	Not present on the Red List of Chemicals (CPA 2009)
End of Life	Degradation	Zinc oxide	1314-13-2	Not present on the Red List of Chemicals (CPA 2009)
End of Life	Degradation	Boric acid	10043-35-3; 11113-50-1	Endocrine Disruptor (CPA 2009)

*The above transformation products were screened against the CPA's table of Red List chemicals (CPA 2009).

Introduction

Zinc borate is used as a flame retardant in conjunction with other chemicals, including antimony trioxide, magnesium hydroxide, alumina trihydrate, and some brominated flame retardants. Zinc borate is used as a flame retardant on commercial furniture, draperies, wall coverings, and carpets (R.C.Kidder, Flame Retardant Chemical Association, unpublished material, April 21, 1998). In addition, zinc borate is used as a fungicide (NAS 2000).

A literature search identified limited publications relating to the toxicity of zinc borate. However, variety of toxicological studies have been performed on various inorganic borates. Longer-term toxicological studies have been reported, and are mainly on boric acid or borax. There is similarity in the toxicological effects of boric acid and borax across different animal species (Hubbard 1998).

Additionally, zinc borate readily breaks down in the stomach to zinc oxide (ZnO) and boric acid (H_3BO_3) (NAS 2000). Therefore, in the absence of data for zinc borate, the data for zinc oxide and boric acid will be substituted. Zinc oxide is used as a pigment in paint, cosmetics, and dental and quick drying cements. Therapeutically, zinc oxide is

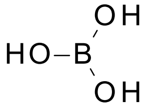
---

[30] A moiety is a discrete chemical entity that is a constituent part or component of a substance. A moiety of concern is often the parent substance itself for organic compounds. For inorganic compounds, the moiety of concern is typically a dissociated component of the substance or a transformation product.

used as an astringent and as a topical protectant. Boric acid is used in enamels, porcelain, soaps, cosmetics, and as an insecticide. Therapeutically, boric acid is used as an astringent and an antiseptic (NAS 2000).

The critical health effect endpoints in several species are male reproductive toxicity and developmental toxicity. Humans would need to consume daily doses of 3.3 g of boric acid (or 5.0 g borax) to ingest the same dose level as the lowest animal NOAEL. No effects on fertility were seen in a population of workers exposed to borates or to a population exposed to high environmental borate levels (Hubbard 1998).

Chemical Structure of Surrogates



Boric Acid (CAS #10043-35-3; 11113-50-1)

O=Zn

Zinc Oxide (CAS #1314-13-2)

Human Health – Tier 1

Carcinogenicity (C) Score (H, M or L): L

Because carcinogenicity data were unavailable for zinc borate, the structurally similar zinc oxide and boric acid were used as surrogates. Zinc borate was assigned a score of Low for carcinogenicity based on negative results from surrogate studies.

Zinc borate

- Not listed as a known carcinogen by IARC, NTP, U.S. EPA, or CA Prop 65.

Zinc oxide

- Not classifiable as to human carcinogenicity due to inadequate evidence in humans and animals (U.S. EPA 2005).

Boric acid

- In long term feeding studies on boric acid and disodium tetraborate decahydrate in both rats and dogs, no carcinogenic effects were observed (Weir and Fisher 1972). In rats, diets contained disodium tetraborate decahydrate or boric acid at 0, 117, 350, and 1,170 ppm boron equivalents for 2 years; these doses were approximately 0, 5.9, 17.5 or 58.5 mg B/kg bw/day. Effects observed in these rat studies included lowered food consumption, retarded body weight gain, course hair coats, haunched position, swollen pads, inflamed bleeding eyes and changes in haematological parameters at the highest doses (58.5 mg B/kg bw/day). Dogs were fed diets containing boric acid (0.033%, 0.067%, 0.2% in diet) or disodium tetraborate decahydrate at (0.051%, 0.103%, 0.309%). No evidence of toxicity was observed. Therefore, additional groups of dogs (4 male and 4 female) were fed diets containing 0.67% boric acid or 1.03% disodium tetraborate decahydrate. The estimated equivalent boron intakes from the boric acid diet were 1.7, 3.8, 10.9 and 40.8 mg B/kg bw/day and from the disodium tetraborate decahydrate diet were 1.9, 3.6, 9.6 and 38.1.mg B/kg bw/day. In dogs, diarrhea was observed in some and soft stools in all dogs at the highest dose tested. Testicular effects were observed in both rats and dogs. Testicular atrophy with some interstitial cell hyperplasia was the critical effect seen in a US National Toxicology Program (NTP) bioassay in mice (dose levels in food 0, 2,500, 5,000 ppm boric acid). No carcinogenic effects were observed at these doses estimated to be equivalent to 78 mg B/kg bw/day and 201 mg B/kg bw/day (NTP 1987). Effects on survival rate and reduced body weight gain were seen at the high doses. The studies carried out are not to modern standards, nor to GLP. However, they are well performed and reported, and are more than adequate to evaluate the carcinogenicity of boric acid and sodium tetraborates. It can be concluded that boric acid and sodium tetraborates are not carcinogenic and there is no concern for a carcinogenic effects in humans (HERA 2005).

Mutagenicity (M) and Genotoxicity Score (H, M or L): L

Because mutagenicity and genotoxicity data for zinc borate are limited, additional data for zinc oxide and boric acid are included. Zinc borate was assigned a score of Low for mutagenicity and genotoxicity based on negative mutagenicity results.

Zinc borate

- Zinc borate did not induce either genotoxic effects or chromosomal aberrations in mutagenicity studies (U.S. EPA 1991).
- In the Salmonella/microsomal assay (Ames assay) for bacterial mutagenic activity, zinc borate did not elicit any mutagenic response in *Salmonella* tester strains when tested either with or without a metabolic activation system (the EPA did not identify specific strains or concentrations) (U.S. EPA 1991).

Zinc oxide

- Several studies were identified that investigated the genotoxicity of zinc oxide. Data on other zinc compounds are relevant for a hazard evaluation based on the assumption that after intake the biological activities of zinc compounds are determined by the zinc cation. Available data indicate that the genotoxicity results vary widely. Conflicting results have been found, even in the same test systems. Overall, the results of the *in vitro* tests indicate that zinc has genotoxic potential. This is based on positive results in mammalian test systems for gene mutations and chromosomal aberrations as well as on the positive *in vitro* UDS test. *In vivo* increases in chromosomal aberrations were found in calcium-deficient mice exposed via the diet as well as in mice with normal calcium status when dosed intraperitoneally. Additionally, negative results were obtained in mice at higher intraperitoneal dose levels. Rats tested negative for chromosomal aberrations after oral dosing, either via gavage or via the diet. The positive result for chromosomal aberrations *in vitro* is considered overruled by negative *in vivo* tests for this endpoint. The positive sperm head abnormality test is considered sufficiently counter-balanced by two negative SLRL tests as well as two negative dominant lethal tests. Moreover, this sperm test is not adequately reported and without details on scoring criteria, interpretation of the observations is rather subjective. In addition, sperm head abnormalities are indicative rather than proof for genotoxicity. Based on the available data there is insufficient ground to classify zinc as genotoxic. It should be noted that the potential to induce gene mutations was not adequately tested *in vivo*. However, there is no clear evidence from the available data that zinc is genotoxic *in vivo* and, without a clear indication for carcinogenicity, guidance for further testing with respect to target tissue is not available (ESIS 2008).

Boric acid

- A number of *in vitro* mutagenicity studies, including bacterial mutation assays in Salmonella typhimurium and Escherichia coli, gene mutation in mammalian cells (L5178Y mouse lymphoma, V79 Chinese hamster cells, C3H/10T1/2 cells), bacterial DNA-damage assay, unscheduled DNA synthesis (hepatocytes), chromosomal aberration and sister chromatid exchange in mammalian cell (Chinese hamster ovary, CHO cells) have been carried out on boric acid, disodium tetraborate decahydrate or disodium octaborate tetrahydrate. No evidence of mutagenic activity was observed (NTP 1987; Haworth et al. 1983; Landolph 1985; Bakke 1991; Stewart 1991).
- No mutagenic activity was seen *in vivo* in a mouse bone marrow micronucleus study on boric acid (O'Loughlin 1991).

Reproductive (R) and Developmental (D) Toxicity Score (H, M or L): *M*

Because reproductive and developmental toxicity data were unavailable for zinc borate, the structurally similar zinc oxide and boric acid were used as surrogates. Zinc borate was assigned a score of Moderate for reproductive and developmental toxicity based on developmental effects reported in rats, mice and rabbits exposed to boric acid (H_3BO_3). The most sensitive species appears to be rats, in which the effects observed at non-maternally toxic doses include a reduction in fetal body weight and minor skeletal variations.

Zinc borate

- No relevant reproductive and developmental toxicity data were identified for zinc borate.

Zinc oxide

- Groups of Sprague-Dawley rats (10/group) were fed diets containing 2,000 or 5,000 mg ZnO/kg feed (calculated to be 150 or 375 mg ZnO/kg bw [≈120 or 300 mg Zn^{2+}/kg bw/day]) from day 0 of gestation to day 14 of lactation, then mothers and remaining pups were killed. The control animals received a basal diet containing 9 mg Zn^{2+}/kg feed. Maternal weight, daily food intake, duration of gestation, and the number of viable young/litter were not affected. No external malformations were seen. Two females at 5,000 mg/kg feed had all stillborn litters containing edematous pups. At 2,000 mg/kg feed, 4 stillborn pups (not edematous) were observed. Dry liver weights of pups (newborn and 14 days old) were decreased at 5,000 mg/kg feed. A dose-related increase in zinc content and a dose-related decrease in iron content were observed. The livers of newborns of zinc-treated dams, however, contained significantly more iron than the controls. This was not observed in the 14-day old pups. The copper levels in the liver were significantly lower only in the newborns of the 5,000 mg/kg level. After 14 days the copper concentrations were significantly lower in all treated pups (Ketcheson et al. 1969).
- Bleavins et al. (1983) exposed groups of mink (11 females and 3 males/group) to a basal diet (containing 20.2 mg Zn^{2+}/kg diet and 3.1 mg Zn^{2+}/kg diet) or to the diet supplemented with 1,000 mg ZnO/kg diet. No maternal effects were seen. All females on the basal diet produced offspring, 8/11 females of the Zn-

supplemented diet group had young. None of the animals (males, females and kits) were sacrificed, so they were only macroscopically examined. The kits were kept on the basal and supplemented diets. The body weight of male kits on the supplemented diet was significantly lower at 12 weeks of age. 8-Week old kits on the supplemented diet showed a significant decrease of the Ht-value, the other blood parameters were comparable to the kits on basal diet. The decreased T-cell mitotic response observed in the Zn-supplemented kits was reversible when the kits were placed on basal diet. Kits (3-4 weeks old) of females fed the Zn-supplemented diet showed effects consistent with copper deficiency, such as grey fur around eyes, ears, jaws and genitals together with hair loss and dermatosis in these areas.

- Hence, with respect to effects on reproduction, zinc deficiency is known to result in impairment of fertility and of fetal development. In humans additional zinc up to 0.3 mg Zn^{2+}/kg bw/day during pregnancy did not result in adverse effects. Available data in animals on zinc excess indicate that adverse effects on fertility and fetal development may occur at dose levels of 200 mg Zn^{2+}/kg bw/day, in conjunction with other effects such as perturbation of parental and fetal copper homeostasis. In humans, a small disturbance (if any) of normal physiology, presumably indicative for copper deficiency, has been demonstrated at zinc excess of 50 and 150 mg Zn^{2+}/day (0.83 and 2.5 mg Zn^{2+}/kg bw/day, respectively), while 150 mg Zn^{2+}/day (2.5 mg Zn^{2+}/kg bw/day) resulted in clinical signs. As the margin between the dose at which in humans clinical signs are manifested and the dose at which in animals reproductive effects have been reported is so high (viz. 80), it is considered unlikely that in humans reproductive effects will occur at exposure levels at which clinical signs are not manifest. Therefore, neither fertility nor developmental toxicity is considered end-points of concern for humans. Based on the available information there is no reason to classify metallic zinc nor any of the zinc compounds considered for reproductive toxicity.

<u>Boric acid</u>

- Effects on the testis have been observed in both sub-chronic and chronic studies in three species: rats, mice and limited studies in dogs. In rats, a single dose of 175 mg B/kg bw was found to cause reversible disruption of tubular spermiation (Linder et al. 1990), although no such effects were observed after a single dose of 350 mg B/kg (2,000 mg boric acid/kg) (Bouissou and Castagnol 1965). The effects tend to be similar in all three species, although most data comes from rat studies. The reproductive effects in rats at lower doses and shorter time periods start with reversible inhibition of spermiation. Early effects were seen after 14 days treatment, at doses around 39 mg B/kg, (217 mg boric acid/kg bw/day) but at a lower dose of 26 mg B/kg (149 mg boric acid/kg bw/day) the effects take about 28 days to manifest (Ku et al. 1993). In a rat three generation study of boric acid and disodium tetraborate decahydrate, doses equivalent to 58.5 mg B/kg bw/day led to testicular atrophy, degeneration of seminiferous tubules, reduced sperm count and a reduction in fertility, with a NOAEL of 17.5 mg B/kg bw/day (Weir and Fisher 1972). Similar results were seen in a two-year study of boric acid and disodium tetraborate decahydrate at 58.5 mg B/kg bw/day where the NOAEL was also 17.5 mg B/kg bw/day (Weir and Fisher 1972). In male rats fed disodium tetraborate decahydrate for either 30 or 60 days at 100 or 200 mg B/kg bw/day testis weight was reduced, testicular germ cells were depleted, selected testicular enzymes were affected and fertility was reduced. The NOAEL was 50 mg B/kg bw/day (Lee et al. 1978). As might be expected, while recovery from inhibition of spermiation occurred at the lower doses, there was no recovery from testicular atrophy when the germ cells were lost.

- Data in dogs derives from two very limited and unreliable two-year dietary studies. Unfortunately, the published study does not accurately reflect the original study reports (Weir and Fisher 1972). In the published paper, the authors estimated the dietary intakes from standard intake figures. However, actual dietary intake was reported in the original study reports allowing a more accurate measure of the dietary intake to be made which are used in this review. Groups of only four male dogs were fed either boric acid or disodium tetraborate decahydrate at doses up to 10.2 mg B/kg bw/day (62.4 mg boric acid/kg bw/day and 84.7 mg disodium tetraborate decahydrate/kg bw/day) in one study and 39.5 mg B/kg bw/day (233.1 mg boric acid/kg bw/day and 373.2 mg disodium tetraborate decahydrate/kg bw/day) in a second study. The animals were sacrificed at various time periods such that observations were reported on only 1 or 2 animals. At 39.5 mg B/kg bw/day, testicular atrophy was observed, however the effects in the only one disodium tetraborate decahydrate treated dog investigated at 38 weeks were less severe than those seen in the control dog. Also, testicular atrophy was present in three out of four control dogs, so that the significance of the effect in the treated animals is difficult to assess. One boric acid treated and one disodium tetraborate decahydrate treated dog were allowed to recover for three weeks. Some recovery was observed in each dog. Minor histopathological changes such as decreased spermatogenesis remained which was less obvious in the disodium tetraborate decahydrate treated dog. The NOAEL was deemed to be the equivalent of 10.2 mg B/kg bw/day by the authors (Weir 1966 a,b; 1967 a,b; Weir and Fisher 1972). For the reasons given above (effects in control animals, insufficient group sizes, inaccurate dose reporting), this data is not reliable for risk assessment, but it does confirm the effects seen in other species. Due to the acute toxic effects of borates in dogs, had the LOAEL doses been administered as a single dose (i.e. by gavage) then vomiting would have occurred and the study would not have been possible.
- A dose-related effect on the testis was observed in rats and mice with confirmation from limited and unreliable studies in dogs. Effects start with reversible inhibition of spermiation after 14 days treatment, at doses around 39 mg B/kg, (217 mg boric acid/kg bw/day) although at a lower dose of 26 mg B/kg (149 mg boric acid/kg bw/day) the effects take about 28 days to manifest. Higher doses (58.5 mg B/kg bw/day and above) led to testicular atrophy, degeneration of seminiferous tubules, reduced sperm count and a reduction in fertility. No recovery from testicular atrophy was observed when the germ cells were lost. The NOEL for this endpoint is 17.5 mg B/kg corresponding to 100 mg boric acid/kg/day; 155 mg disodium tetraborate decahydrate/kg and 118 mg disodium tetraborate pentahydrate/kg (HERA 2005).
- The majority of developmental toxicity studies have been carried out in rats exposed to boric acid (H_3BO_3). In two separate dietary studies performed in the

same laboratory, groups of rats were given dose levels of approximately 3.3, 6.3, 9.6, 13.7, 25, 28 and 59 mg B/kg bw/day on gestation days 0-20 and 94 mg B/kg bw/day on gestation days 6-15 in feed. The NOAELs for maternal toxicity and developmental effects were 13.7 mg/kg bw/day and 9.6 mg B/kg bw/day (equivalent to 54.9 mg H_3BO_3/kg-bw)[31], respectively. A reduction in food intake and an increase in relative liver and kidney weight and a reduction in maternal body weight gain at higher doses indicated maternal toxicity. At non-maternally toxic doses, there was a reduction on fetal weight and some skeletal variations and malformations (increase in wavy ribs and short rib XIII and a decreased incidence of rudimentary extra rib on lumbar 1), which had reversed by postnatal day 21 at 13.7 mg B/kg bw/day also, with the exception of short rib XIII, had reversed at 28.6 mg B/kg bw/day in a study designed to look at postnatal recovery (Price et al. 1990, 1996). At higher maternally toxic doses, other indications of developmental effects were observed, including resorptions and visceral malformations (enlarged lateral ventricles; cardiovascular effects; anophthalmia and microphthalmia and short and curly tails). However, these are likely to have been secondary to the maternal toxicity (Price et al. 1990, 1996; Heindel et al. 1992).

- Similar findings were observed in mice receiving estimated doses of 0, 43, 79, and 175 mg B/kg bw/day on gestation days 0-20 in feed. Maternal toxicity was indicated by a dose related incidence of renal tubule dilation/regeneration and at the highest dose increases food and water consumption in late gestation and in the relative kidney weight. A NOAEL was not determined for maternal toxicity. The key developmental effects observed were similar to those seen in rats i.e. a reduction in foetal body weight at the mid dose (79 mg B/kg) and an increase in skeletal variations and malformations (missing lumbar vertebrae, fused vertebral arches and short rib XIII) and resorptions at the highest, more maternally toxic dose. The NOAEL for developmental effects in mice was 43 mg B/kg bw/day (Heindel et al. 1992); however, this dose was also a maternally toxic dose.
- In rabbits receiving estimated doses of 0, 11, 22 and 44 mg B/kg bw/day by gavage on gestation days 6-19 maternal toxicity was indicated by effects such as an increase in relative kidney weight, increase food intake, vaginal bleeding and an increase in corrected weight gain. Developmental effects were seen only at the top dose, where the majority of the embryos were resorbed and malformations were primarily visceral (major heart and/or great vessel defects); however, these effects are likely to be secondary to the maternal toxicity. The only skeletal effect observed was a decreased incidence of rudimentary extra rib on lumbar 1 which was not considered biologically significant. The NOAEL for both maternal and developmental toxicity in the rabbit was 21.8 mg B/kg bw/day (Price et al. 1991).
- Developmental effects have been observed in three species, rats, mice and rabbits. The most sensitive species appears to be rats, in which the effects observed at non-maternally toxic doses include a reduction in fetal body weight and minor skeletal variations which, with the exception of short rib XIII, had reversed by 21

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[31] $\frac{9.6\text{ mg B}}{\text{kg bw}} * \frac{\text{g B}}{1{,}000\text{ mg B}} * \frac{\text{mol B}}{10.811\text{ g B}} \frac{\text{mol } H_3BO_3}{\text{mol B}} \frac{61.83302\text{ g } H_3BO_3}{\text{mol } H_3BO_3} \frac{1{,}000\text{ mg } H_3BO_3}{\text{g } H_3BO_3} 54.9 \frac{\text{mg } H_3BO_3}{\text{kg bw}}$

days post natal. The NOAEL for developmental effects is 9.6 mg B/kg (HERA 2005).

Endocrine Disruption (ED) Score (H, M or L): *M*

Because endocrine disruption data were unavailable for zinc borate, the structurally similar zinc oxide and boric acid were used as surrogates. Zinc borate was assigned a score of Moderate for endocrine disruption based on suggestive animal studies for boric acid and the presence of boric acid on the European Union Priority List of Suspected Endocrine Disruptors.

Zinc borate

- Not listed as a potential endocrine disruptor on the EU Priority List of Suspected Endocrine Disruptors.
- Not listed as a potential endocrine disruptor on the OSPAR List of Chemicals of Possible Concern.
- Not listed as a potential endocrine disruptor on the Red List of Chemicals (CPA 2009).

Zinc oxide

- No relevant data were identified.

Boric acid

- The majority of toxicological studies have been reported on boric acid (H_3BO_3) or disodium tetraborate, known as borax ($Na_2B_4O_710H_2O$). The inorganic borates display low acute toxicity orally, dermally or by inhalation. They are either not irritant or mild skin and eye irritants. They are not skin sensitizers, nor are they mutagenic or carcinogenic. In sub acute and chronic studies of boric acid in rats, mice, and dogs, the target organ is the testis. Effects on reproductive organs in females were seen, but at higher doses than in males. Effects on fertility were also seen in rats in a three-generation study and in mice in a continuous breeding study. The testicular effects observed include reduction in sperm count, inhibition of spermiation, and testicular atrophy. Reversal of inhibition of spermiation and reduced sperm count in rats was seen after removal of treatment at 38 mg B/kg bw/day (equivalent to 217 mg/kg bw/day boric acid). Minimal inhibition of spermiation was observed at 26 mg B/kg bw/day. A dose of 17 mg B/kg bw/day in male rats (equivalent to 97 mg/kg bw/day boric acid) was the NOAEL. Developmental toxicity has also been demonstrated in mice, rats and rabbits, with rats the most sensitive species. Administration of a wide range of doses of boric acid to pregnant rats for the whole of gestation has shown that at doses of 330 mg/kg bw/day (equivalent to 58 mg B/kg bw/day) and above, there is a high resorption rate and retardation of fetal development. At a lower dose of 28 mg B/kg bw/day, the only effects observed were reduced fetal weight and short 13th rib and wavy rib. These effects disappear if the pups are allowed to be delivered and reared to weaning. The NOAEL was 9.6 mg B/kg bw/day (equivalent to 54 mg/kg bw/day boric acid) (Hubbard 1995).
- To assess whether or not male reproductive toxicity can be evaluated in a 2 week administration study, boric acid was administered daily by oral gavage to male Jcl:Wistar rats at dosage levels of 0, 300, and 500 mg/kg for 2 and 4 weeks, and the results obtained with the 2 different treatment schedules were compared. After a 2 week administration, decreased testis weights were observed in the 500

mg/kg group. Histopathologically, exfoliation of round spermatids, retention of step 19 spermatids, and increased numbers of residual body-like structures in the seminiferous tubules and cell debris in the cranial epididymal ducts were observed in the 300 and 500 mg/kg groups. Distorted cytoplasmic lobes of step 19 spermatids, debris in the seminiferous tubules, and focal atrophy of the seminiferous tubules with multinucleated giant cells formation and necrosis of spermatocytes were also observed in the 500 mg/kg group. After a 4 week administration, testis and epididymis weights were decreased in the 300 and 500 mg/kg groups. Histopathological changes in the 300 mg/kg group were similar to those found in the 300 and 500 mg/kg groups after a 2 week administration. Diffuse atrophy of the seminiferous tubules was additionally observed in the 500 mg/kg group. These results suggest that 2 week is a sufficient treatment period for the detection of the testicular toxicity caused by boric acid (Fukuda et al. 2000).

Neurotoxicity (N) Score (H, M or L): nd

Because neurotoxicity data were unavailable for zinc borate, the structurally similar zinc oxide and boric acid were used as surrogates. No relevant neurotoxicity data were identified for zinc borate, zinc oxide, or boric acid.

Zinc borate

- Not classified as a developmental neurotoxicant (Grandjean and Landrigan 2006).
- Not listed as a potential neurotoxicant on the Red List of Chemicals (CPA 2009).

Zinc oxide

- Special studies were conducted to examine the morphological and histoenzymatic changes of the brain. Twelve Wistar rats were given daily doses of 100 mg ZnO (ca. 600 mg ZnO/kg bw ≈w480 mg Zn2+/kg bw) intragastrically for 10 consecutive days. A control group was included. After 10 days the rats were sacrificed and the brains were examined for morphological and histoenzymatic changes. Morphological changes included degenerative changes of neurocytes, accompanied with moderate proliferation of the oligodendroglia, and glial proliferation in the white matter. Furthermore, endothelial edema was observed in the small arterial and capillary walls. Histoenzymatic changes included decreased activities of ACP (acid phosphatase), ATPase (adenosinetriphosphatase), AChE (acetylcholine esterase), and BChE (Butyrylthiocholineesterase). The activities of TTPase (thiamine pyrophophatase) and NSE (non-specific esterase) were increased. No details on quantitative aspects of enzymatic changes were given. No change was seen in the alkaline phosphatase. The authors indicated that observed morphological and histoenzymatic changes were unspecific, undistinctive and most likely reversible (Kozik et al. 1980). Examination of the neurosecretory function of the hypothalamus and the hypophysis in these animals showed an increased neurosecretion in cells of the supraoptic and paraventricularnucleus of the hypothalamus along with a declined neurosecretion in the hypophysis and an enhanced release of antidiuretic hormone in the neurohypophysis (Kozik et al. 1981). It is not clear whether these observations represent an adverse effect of zinc on the brain or whether they are secondary to changes somewhere else in the body.

Boric acid

- No relevant neurotoxicity data were identified for boric acid.

Human Health – Tier 2

Acute Mammalian (AT) Toxicity Score (H, M or L): L

Zinc borate was assigned a score of Low for acute mammalian toxicity based on oral and dermal LD50 values greater than 2,000 mg/kg-bw. This score is based on data from 3 routes of exposure in two different species of animals.

- *Oral*: An LD_{50} of >10,000 mg/kg was determined in rats (U.S. EPA 1991).
- *Oral*: An LD_{50} of >5,000 mg/kg was determined in rats (Cerven 1992).
- *Oral*: An LD_{50} of >10,000 mg/kg was determined in rats (Daniels et al. 1969).
- *Dermal*: An LD_{50} of >10,000 mg/kg in both male and female albino rabbits (U.S. EPA 1991).
- *Inhalation*: An LD_{50} of > 5 mg/L was determined (species unspecified) (EFRA 2006).

Corrosion/Irritation (Skin/ Eye) (Cr) Score (H, M or L): M

Zinc borate was assigned a score of Moderate for corrosion/irritation as both dermal and ocular irritation have been reported.

- *Dermal*: Contact with skin causes irritation (HSDB 2003).
- *Dermal*: The Primary Irritation Index of zinc borate in rabbits was found to be 0. Therefore, it is not considered to be an irritant or corrosive (U.S. EPA 1991).
- *Ocular*: Contact with eyes causes irritation (HSDB 2003).
- *Ocular*: Zinc borate produced only mild conjunctivitis in albino rabbits in the eye irritation test and is not considered to be an irritant or corrosive (U.S. Borax 1996).
- *Ocular*: Zinc borate was shown to be an eye irritant producing mild conjunctivitis in albino rabbits (U.S. EPA 1991).
- *Inhalation*: Inhalation of dust may irritate nose and throat (HSDB 2003).
- Zinc borates are not skin or eye irritants (no species or doses provided) (EFRA 2006).

Sensitization (Sn) Score (Skin and Respiratory) (H, M or L): L

Because sensitization data were sparse for zinc borate, the structurally similar zinc oxide and boric acid were used as surrogates. Zinc borate was assigned a score of Low for sensitization based on negative sensitization test results in surrogates.

Zinc borate

- *Dermal*: Zinc borate was negative in the guinea pig sensitization test (U.S. Borax 1996).

Zinc oxide

- The skin sensitization potential of zinc oxide (99.69% purity) was investigate in female Dunkin Hartley guinea pigs in two well-performed maximization tests, conducted according to Directive 96/54/EC B.6 and OECD guideline 406. Based on the results of a preliminary study, in the main studies experimental animals (10 in each test) were intradermally injected with a 20% concentration and epidermally exposed to a 50% concentration (i.e. the highest practically feasible concentration). Control animals (5 in each test) were similarly treated, but with vehicle (water) alone. Approximately 24 hours before the epidermal induction exposure, all animals were treated with 10% SDS. Two weeks after the epidermal application, all animals were challenged with a 50% test substance concentration and the vehicle. In the first study, in response to the 50% test substance concentration skin reactions of grade 1 were observed in 4/10 experimental animals 24 hours after the challenge (40% sensitization rate), while no skin reactions were evident in the controls. In contrast, in the second study no skin reactions were evident in the experimental animals (0% sensitization rate), while a skin reaction grade 1 was seen in one control animal. The skin reaction observed in one control animal is probably a sign of non-specific irritation (Van Huygevoort, 1999b1; 1999b2). In a third, well-performed maximization test, conducted according to the same guidelines and with the same experimental design, another analytical grade zinc oxide was tested (Zincweiß Pharma A; purity 99.9%). The only difference with the studies described above was the intradermal induction concentration, which was 2% as for Zincweiß Pharma A this was considered the highest concentration that could reproducibly be injected. In this test, no skin reactions were evident in both experimental and control animals, hence a 0% sensitization rate for Zincweiß Pharma A. White staining of the treated skin by the test substance was observed in some animals 24 and 48 hours after challenge (Van Huygevoort 1999i).

- In a human patch test performed with 100 selected leg-ulcer patients, 11/100 patients gave an allergic reaction with zinc ointment (60% ZnO and 40% sesame oil). However, 14/81 patients gave a positive response when treated with sesame oil alone (Malten and Kuiper 1974). This study does not give any indication for a skin sensitizing potential of zinc oxide in humans. Söderberg et al. (1990) studied the effect of zinc oxide on contact allergy to colophony. With 14 patients with earlier history of moderate patch test reactions to colophony a patch test with 10% ZnO (2.3 mg Zinc/cm^2) with and without colophony was performed. No positive response was observed in the 14 patients when only a 10% solution of zinc oxide was used. The addition of zinc oxide to colophony decreased the allergic reaction induced by colophony.
- The data submitted fulfill the base-set requirements for skin sensitization testing. While some studies with guinea pigs produced conflicting results, the weight of evidence does not indicate that zinc oxide is a very potent sensitizing agent in animals, if any. In addition, the results of human patch tests do not indicate that zinc oxide acts as a sensitizing agent in humans, either. Zinc oxide does not have to be classified/labeled for skin sensitization. This is supported by the fact that zinc compounds, especially zinc oxide and zinc distearate, have been used for over decades in a variety of pharmaceutical and cosmetic products (some of them even dermatological preparations against skin irritation) without any such reported effects (ESIS 2008).

Boric acid

- Boric acid and sodium tetraborates are not skin sensitizers in either human and animal studies (Wnorowski 1994a,b,c; Bruze et al.1995).

Systemic/Organ (ST) Toxicity Score (includes organ effects and immunotoxicity) (H, M or L): M

Because systemic toxicity data were sparse for zinc borate, the structurally similar zinc oxide and boric acid were used as surrogates. Zinc borate was assigned a score of Moderate for systemic toxicity based on an oral LOAEL for systemic effects of 81.3 mg ZnO/kg bw.

Zinc borate

- In animal feeding studies, high levels of boric acid displays effects on fertility (rats, mice. dogs) and development (rats, mice, rabbits). High levels of zinc salts do cause adverse effects on fertility and development in animals, but at doses that perturb copper homeostasis resulting in other adverse effects. The doses administered were many times in excess of those which humans would be exposed and therefore the effects would not be seen in humans. A human epidemiology study on workers exposed to boric acid and sodium borates indicated no effect on fertility, while a study in pregnant women taking zinc supplements found no adverse effects. Zinc is an essential element for normal fetal development. Also, there is increasing evidence that boron is nutritionally important and may be essential for mammals (EFRA 2006).

Zinc oxide

- Four groups of ferrets (3-5/group) were given 0, 500, 1,500, or 3,000 mg zinc oxide/kg feed (equivalent to be 0, 81.3, 243.8 or 487.5 mg ZnO/kg bw, respectively. At the highest dose level (487.5 mg ZnO/kg bw) all animals (3) were killed in extremis within 13 days. Macroscopic examination showed pale mucous membranes, dark colored fluid in the stomach, blood in the intestines, orange colored liver and enlarged kidneys showing diffuse necrosis, hemorrhages in the intestine and a severe macrocytic hypochromic anaemia. Histology showed nephrosis and extramedullary hematopoesis in the spleen. At the mid dose level of 243.8 mg ZnO/kg bw, the animals (4) were killed on day 7, 14 and 21 (1/2 in extremis) showing poor condition. Macroscopy showed pale livers with fatty infiltration and enlarged kidneys. Histology was comparable with the highest dose group. The hemogram showed macrocytic hypochromic anaemia, increased reticulocytes and leucocytosis. At the lowest dose level (81.3 mg ZnO/kg bw), the animals (3) were killed on day 48, 138 and 191, respectively. No clinical signs of toxicity or pathological changes were seen, apart from an extramedullary heamatopoesis in the spleen (Straube et al. 1980).
- Ellis et al. (1984) conducted a 14 day and a 49 day feeding study in 3 different breeds of sheep that were receiving feed containing 31 mg Zn^{2+}/kg feed. The sheep received additional amounts of Zn^{2+} (from ZnO) at dose levels of 261 and 731 (14 day study), or 731 and 1,431 mg Zn^{2+}/kg feed (49-day study). No effects were seen after 261 mg Zn^{2+}/kg feed. In all other groups, pancreatic lesions were seen.
- Administration of 240 mg Zinc (as ZnO)/kg bw for 3 times/week during 4 weeks to 42 castrated sheep resulted in an increased incidence of pancreatic lesions (Smith and Embling 1993).

- Male Hartley guinea pigs were exposed to 0, 2.3, 5.9, or 12.1 mg/m^3 of ZnO (as ultra fine particles with an average diameter of 0.05 µm) 3 hours a day for 1, 2, or 3 consecutive nose-only exposures. Three animals from each group were examined after each exposure period; they were sacrificed and lung tissues were microscopically examined, and the pulmonary lavage fluid was also examined. Exposure to 12.1 mg/m^3 increased the number of nucleated cells in lavage fluid. Exposures to 5.9 and 12.1 mg ZnO/m^3 were associated with increased protein, neutrophils, and activities beta glucuronidase, acid phosphatase, alkaline phosphatase, lactate dehydrogenase, and angiotensin-converting enzyme. The increases were dose dependent and were detectable after the second exposure and generally increased after the third exposure. Significant morphologic damage characterized by centriacinar inflammation in the lung was seen at 5.9 and 12.1 mg/m^3. Minimal changes in neutrophils and activities of lactate dehydrogenase and alkaline phosphatase were seen in the pulmonary fluid at the lowest dose level of 2.3 mg/m^3 after 3 exposures but no morphologic changes were observed at this dose level. Based on these results, 2.3 mg ZnO/ m^3 is considered as a marginal LOAEL in this study (Conner et al. 1988).
- Male Hartley guinea pigs were exposed to 6 mg/m^3 of ultra fine ZnO (average diameter of 0.05 µm) for 3 hours a day for 1 to 5 days by nose-only exposure. A control group was included. After each exposure, 3 animals were sacrificed and lung tissues were microscopically examined. After first, second and third exposure 3 additional animals were sacrificed and their pulmonary lavage fluid was examined. ZnO-exposure increased the total cell count, neutrophils, protein, and the enzyme activities of angiotensin converting enzymes, Acid phosphatase, alkaline phosphatase, and β-glucoronidase. Furthermore, a dose-related centriacinar inflammation was seen after second exposure (Conner et al. 1986).
- Male Hartley guinea pigs were exposed to 0, 2.7, or 7 mg ultra fine (0.05 µm in diameter) ZnO/m^3 3 hours a day for 5 days. Lung function measurements were performed every day after exposure in 5-8 animals. After the last exposure the animals were sacrificed. At the highest exposure level, a gradual decrease in total lung capacity (18%) and vital capacity (22%) was seen during the exposure period. At day 4, the carbon monoxide diffusing capacity dropped to below 30% of the control level. Wet-lung weights were increased with 29%, indicating the presence of edema. Exposures up to 2.7 mg ZnO/m^3 did not alter any parameters measured (Lam et al. 1988).
- Male Hartley guinea pigs (73) were exposed (nose-only) 3 hours a day for 6 days to 5 mg ZnO/m^3 (0.05 µm in diameter). A group of 53 animals served as control group. Lung function tests (in 38 animals) were performed and the respiratory tract of the animals was morphologically examined 1, 24, 48 and 72 hours after the last exposure. Furthermore epithelial permeability (5 animals at 1 and 24 hours) and DNA synthesis in epithelial cells (5 animals at 24, 48 and 72 hours) were determined. Vital and functional residual capacity, alveolar volume and carbon monoxide diffusing capacity were all decreased and did not return to normal values 72 hours after the last exposure. Lung weights were elevated due to inflammation, still present at 72 hours after last exposure (Lam et al. 1985).
- 240 Female Wistar rats (80/group) were exposed by inhalation to 15 mg ZnO/m^3 for 1 hour, 4 hours or 8 hours a day for 5 days a week. 20 Animals/group were

sacrificed after 14, 28, 56, and 84 days and their lungs were examined for zinc content. It appeared that the highest daily exposure time resulted in the highest dry lung weights, independent of the duration of the experiment, while the zinc content remained almost constant. The absolute and relative (relative to dried weights of lung tissue) zinc content in the lungs was influenced by the duration of the experiment. After 84 days exposure the zinc content was significantly higher compared to 14 days exposure, independent of the duration of the daily exposure (Dinslage-Schlünz and Rosmanith 1976).

Boric acid

- A number of studies in which rats were fed boric acid or disodium tetraborate decahydrate in their diet or drinking water for periods of 70 - 90 days indicated that the main target organ for toxicity is the testis. As well as testicular atrophy, animals receiving doses of 88 mg B/kg bw/day for 90 days in their diet exhibited weight loss and, at higher doses, rapid respiration, inflamed eyes, swollen paws and desquamation of the skin on the paws (Weir and Fisher 1972; NTP 1987). The main effects observed were on the testis.

Ecotoxicity

Acute Aquatic (AA) Toxicity Score (H, M or L): H

Because acute aquatic toxicity data were limited for zinc borate, the structurally similar zinc oxide and boric acid were used as surrogates. Zinc borate was assigned a score of High for acute aquatic toxicity based on the risk phrases: R50-R53.

- Zinc borates are classified as Dangerous to the Environment, R50/R53, Very toxic to aquatic organisms/May cause long-term effects in the aquatic environment. Zinc borates are considered as ‗sparingly soluble salts' based on their toxicity. However, both boron and zinc are essential micronutrients for the healthy growth of plants and other aquatic organisms (EFRA 2006).

Zinc oxide:

- Associated with risk phrases R50, R51, R52, and R53 (ESIS 2008).
- *Algae*: The two tests with the unicelllular alga *Pseudokierchneriella subcapitata* (formerly known as *Selenastrum capricornutum*), in which two different grades of ZnO were tested (―Red seal grade", purity 99.77%, and ―EPM-grade", purity 99.37%), resulted in 72-h ErC_{50} values for dissolved zinc of 135 and 136 µg Zn/l, respectively, for endpoint specific growth rate. The 72-h NOErC values for dissolved zinc were 8 and 24 µg/l, respectively (Table 3.3.1: LISEC, 1997; Van Ginneken 1994a). These NOEC values suggest that Red seal-grade ZnO may be somewhat more toxic than EPM-grade ZnO, but because of some differences between the two tests (using either statistics to derive the NOEC or using the lowest test concentration that resulted in less than 10% effect as NOEC; and either measuring dissolved zinc in the stock solution or in the test waters) and the small difference between the NOEC values, a firm conclusion cannot be drawn. Although red-seal grade ZnO and EPM-grade ZnO both have a high purity, the former contains somewhat less impurities (soluble salts) and is somewhat less soluble than the latter (see also footnote 7 below Table 3.3.1). Based on these characteristics, a somewhat lower toxicity could be predicted for Red-seal ZnO

compared to EPM-grade ZnO, which seems to be not in agreement with the above test results. It is noted that similar growth inhibition tests with the same algal species have been conducted with either a soluble zinc compound or with zinc metal powder (see Table 3.3.2.a and Table 3.3.2.d, respectively, in Annex 3.3.2.A of the Risk Assessment Report on Zn metal). These tests and the above tests with ZnO, all using soft to very soft artificial test media, resulted in comparable NOEC values if expressed as dissolved zinc, i.e. NOEC values in the range of 5-50 µg/l, regardless whether a soluble or ―insoluble" test compound was used.

- *Invertebrates*: A short-term *Daphnia magna* immobilization test with ―EPM-grade" ZnO (purity 99.37%) resulted in a 48-h EC$_{50}$ for dissolved zinc of 1,760 µg/l and a 48-h NOEC for dissolved zinc of 280 µg/l (Table 3.3.1: Van Ginneken 1994b). It is noted that the 48-h NOEC of 280 µg/l from this short-term test is within a factor of 2 of a number of NOEC values (endpoints: survival, reproduction and/or growth) derived in longterm *D. magna* tests in which a soluble zinc salt was used as test compound (see Table 3.3.2.a in Annex 3.3.2.A of the Risk Assessment Report on Zinc metal).
- *Fish*: In a 96-h acute toxicity test with fish *Brachydanio rerio* (test compound ―EPM-grade" ZnO, purity 99.37%), no effect was found for dispersed ZnO at 100 mg ZnO/l (limit test), thus the 96-h EC$_{50}$ is >100 mg ZnO/l, nominal concentration, equivalent to >80 mg Zn/l. The actual dissolved zinc concentration in this ZnO dispersion was 4,700 µg Zn/l (Table 3.3.1: Van Woensel 1994b).

Boric acid

- A summary of appropriate acute test results are detailed in Table 14. Eisler (2000) and Dyer (2001) have compiled numerous literature values. The most sensitive tests report that acute effects on fish are in the range of 10-20 mg-B/L although the quality of these studies was rated low (Reliability code 4). The lowest daphnid acute value is 133 mg-B/L. Algal and microbial inhibition studies (Table 15) suggest less toxicity: Selenastrum growth was not affected at 93 mg-B/L and activated sludge respiration showed minimal effects at 683 mg/L boric acid (119 mg-B/L).
- Other results showed substantially higher values (less toxicity) with fish acute values often exceeding 100 mg-B/L. Juveniles and fry appear to be the most sensitive fish life-stage (Hamilton 1995; Hamilton and Buhl 1990).
- Aquatic studies have been used to create species sensitivity distributions (SSD). SSD incorporate all available information into a summary statistic by calculating a designated percentile of the distribution, such as the 5th percentile. Such values indicate a concentration that is predicted to protect 95% of all species (included those not tested) (Cardwell et al. 1993). Dyer et al. (2001) calculated the Acute 5th percentile concentration for aquatic species. Using the procedure of Aldenberg and Slob (1993), the acute 5th percentile SSD concentration is 43 mg-B/L (246 mg-boric acid/L). Using a similar procedure of Stephan et al. (1985) produces a similar value, 46 mg-B/L (263 mg-boric acid/L).

Chronic Aquatic (CA) Toxicity Score (H, M or L): nd

Because chronic aquatic toxicity data were unavailable for zinc borate, the structurally similar zinc oxide and boric acid were used as surrogates. No relevant chronic aquatic toxicity data were identified for zinc borate, zinc oxide, or boric acid.

Zinc borate

- No relevant data were identified.

Zinc oxide

- No relevant chronic aquatic toxicity data were identified for zinc oxide.

Boric acid

- No relevant chronic aquatic toxicity data were identified for boric acid.

Environmental Fate

Persistence (P) Score (vH, H, M, or L): nd

Because persistence data were unavailable for zinc borate, the structurally similar zinc oxide and boric acid were used as surrogates. No relevant persistence data were identified for zinc borate, zinc oxide, or boric acid.

Zinc borate

- No relevant persistence data were identified for zinc borate.

Zinc oxide:

- No relevant persistence data were identified for zinc oxide.

Boric acid:

- No relevant persistence data were identified for boric acid.

Bioaccumulation (B) Score (vH, H, M, or L): L

Zinc borate was assigned a score of Low for bioaccumulation based on professional opinion.

- Zinc borate has a low bioaccumulation potential. Additionally, Firebrake ZB (zinc borate) will undergo hydrolysis in water to form boric acid and zinc hydroxide. Neither of this substances will biomagnify through the food chain (20 Mule Team 2002).

Physical Properties

Explosivity (Ex) Hazard Rating (H, M or L): L

Zinc borate was assigned a score of Low for explosivity as no basis for concern was identified.

- Not explosive (20 Mule Team 2000).

Flammability (F) Hazard Rating (H, M or L): L

Zinc borate was assigned a score of Low for flammability as no basis for concern was identified.

- NFPA rating of 0 assigned for flammability (i.e. zinc borate is not flammable) (Fisher Scientific 2007).

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