



Flame-O 1000™

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Executive Summary

The employees at KSMH have created a new phosphorus based flame-retardant called Flame-O 1000™. This flame-retardant was created in response to the current and future ban of penta- and octa-bromodiphenyl ethers. Great Lakes Chemical primarily produces these two flame-retardants domestically. Because they are the primary producers of the two chemicals, this voluntary phase out is a preemptive ban. The two chemicals are being banned because of the suspected toxins that form as byproducts: dioxins and furans.

Flame-O 1000™ lacks aromatic rings and halogens, the primary causes for the creation of the toxins. Like other phosphorus flame-retardants, Flame-O 1000™ acts in the solid phase and creates a layer of char on the material it is protecting. This layer of char prevents the release of flammable vapors, which lowers the temperature of the fire and slows the combustion cycle. The two chemicals being phased out work in the vapor phase, by releasing bromine free radicals, which bond to the oxygen in the air, which decreases the fuel of the fire. By decreasing the fuel of the fire, the fire slows, which in turn, lowers the heat of the fire. This entire process is a cyclic reaction to slow the combustion cycle.

KSMH created Flame-O 1000™ through a model, which carefully analyzed the properties that make a molecule flame resistant. These properties include low vapor pressure at high temperatures, a high heat of combustion and a decomposition temperature fifty degrees Celsius below that of the material it is protecting, just to name a few. Flame-O 1000™ was created through molecular discovery after pre-existing products were examined.

KSMH executed an experiment designed to evaluate the performance of Flame-O 1000™ as a flame-retardant in polypropylene. The experiment mimicked the 94HB Horizontal Burn Test. Flame-O 1000™ was applied to the polypropylene as an internal additive and as a coating. From the experiment, KSMH was able to determine that Flame-O 1000™ is an efficient flame-retardant and that the best application should be as an internal additive.

A market analysis was performed, and it was estimated that there would be a hole of \$85,800,000 left in the brominated flame-retardant market after penta- and octa-bromodiphenyl ethers are banned. It was projected that Flame-O 1000™ would fill 3.5% of this hole (a production of 1,850,000 kg/year), with hopes of entering into the phosphorus market as well. The 3.5% of market capture was determined by maximizing profit (NPW) with the lowest risk possible.

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1.0 Introduction

1.1 Dangers of Fire

Domestic property damage resulting from fire averages over \$11 billion annually, according to the National Fire Protection Association. In residential fires in 2001, over 3,100 people lost their lives and another 16,000 were injured. Surveys have shown that most people believe that they are safest from fire when they are in their homes, when actually, 76% of all US structural fires in the year 2001 were residential. Additionally, 64% of 2001 property damages were reported from residential fires¹. Statistically, people who are at the highest risk of injury in a fire are the elderly and children under the age of five. All these statistics emphasize that in order to protect our children, elders, and property, the demand for fire safety has become a necessity. The government has issued strict fire prevention policies that require the use of flame-retardants in many household products and materials. As a result, the number of casualties and amount of property damages from residential fires has gotten progressively lower over the past 25 years².

1.2 Importance of Flame-Retardants

Flame-retardants save lives and property and provide safer materials without compromising performance. The main effect is to reduce the likelihood of fire starting by providing increased material resistance to ignition. If in fact ignition does occur, good flame-retardants are also designed to delay the spread of flames. This provides extra time in which either the fire can be extinguished or an escape can be made³.

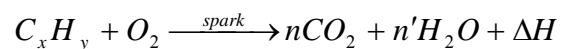
1.3 How Flame-Retardants Work

A flame-retardant is a chemical added to combustible materials to render them more resistant to ignition. The flame-retardants are additives that are applied either during the substrate's manufacturing process or as a coating, which adheres to the substrate's surface. They help prevent fires from starting and spreading by interfering with the combustion and pyrolysis reactions (explained in detail in Section 1.4). There are four major 'families' of flame-retardants, each using different mechanisms. The essential function of any family is to limit the factors that contribute to the spread of flames; decreasing reactant concentrations or reducing the heat generated by the fire. Details of how each family works are covered in Section 2. In general, a flame-retardant molecule makes use of its structural and thermodynamic properties to prevent or delay the spread of fires.

1.4 The Combustion Cycle

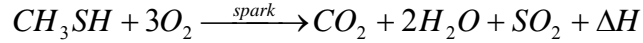
1.4.1 General Combustion

The combustion reaction is the process by which flammable materials are decomposed to release energy in the form of heat and light, i.e., fire. A tremendous amount of energy is required to initiate the combustion reaction for most materials. As such, the energy released from one combusting molecule is usually the activation energy for the next molecule to combust. This gives rise to a cyclical release and use of energy that continues until the flammable material is entirely consumed. For the combustion of hydrocarbons, the reaction proceeds as follows:

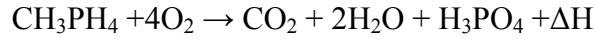


The products of pure hydrocarbon combustion are always carbon dioxide, water, and energy on the magnitude of 1000 – 10,000 KJ/mole⁴. This energy released by combustion raises the temperature of the products of combustion. Several factors and conditions control the level of combustion in an internal combustion engine to provide force and keep efficient operating conditions. The temperature attained depends on the rate of release and dissipation of the energy and the quantity of combustion products.

The most available source of oxygen is air, but because air also contains vast quantities of nitrogen, nitrogen becomes the major constituent of the products of combustion. The rate of combustion may be increased by finely dividing the fuel to increase its surface area and hence its rate of reaction, and by mixing it with the air to provide the necessary amount of oxygen to the fuel. The combustion reaction may also be considered a free-radical reaction: diatomic oxygen breaks into O· radicals in order to attack the hydrocarbon structure. The action of these oxygen radicals, in turn, forms H· and OH· radicals while these molecules are in the gas phase. These high-energy radicals, when uninhibited, increase both the temperature of the flames and the rate at which the fire spreads. The product water is the combination of the H· and OH· radicals after transferring heat to the combusting material⁵. For substituted hydrocarbons, which have non-hydrogen attachments to the carbon chain, the products will also include an oxidized form of the flammable substitutions and the remains of the inflammable portions of the material. For example, the combustion of methyl sulfide gives rise to SO_2 :



Combustion of phosphorus:



1.4.2 Combustion of Different Materials:

If volatile gases are mixed with air and heated by an external heat source to the ignition temperature, exothermic reactions known as combustion begin. If the burning mixture accumulates enough heat to emit radiation in the visible spectrum, the phenomenon is known as flaming combustion⁵. Since the flammable source is already in the vapor phase, the substance is consumed much more rapidly than solids or liquids.

When liquids burn, the liquid phase will absorb its latent heat of vaporization from the pyrolysis reactions until the material is completely vaporized. This serves to remove heat from the pyrolysis zone, thereby slowing down the pyrolysis reactions⁵. Once the material is in the vapor phase, the combustion proceeds in similar fashion to the gas burning discussed above.

1.4.3 Polymeric Plastic Combustion

In the uninhibited combustion of polymer plastics, which are often composed of substituted hydrocarbons, the combustion reaction takes place in the vapor phase. The process by which the solid polymer is transformed into flammable vapors is called pyrolysis. Pyrolysis is similar to combustion in that it is a decomposition

reaction; however, it is an endothermic process (bond breaking and rearranging) and oxygen is not required for product formation. As such, pyrolysis can be considered the initiating reaction in the consumption of plastics by fire. The products of pyrolysis can be found in all three phases. The vapor phase products are a mixture of flammable and inflammable molecules. The liquid products are later volatilized into either flammable or inflammable vapors after absorbing energy from the flames. The solid product is usually a film or residue consisting of fixed carbon, ash, inorganic salts and metal oxides, etc. Optimal thermodynamic conditions for pyrolysis reactions of plastic involve operating temperatures above 430°C and a pressure greater than atmospheric^{6&7}. Upon ignition, a cyclical pyrolysis-combustion process is set in motion; see Figure 1. “Pyrolysis of the polymer is reinforced by thermal feedback which fuels the flame at an increasing level. The diffusion flame is supported by high energy H· and OH· radicals who confer a high velocity on the flame front⁸.” An uninhibited pyrolysis-combustion process will continue as long as there is polymer surface area exposed to the high energy flames.

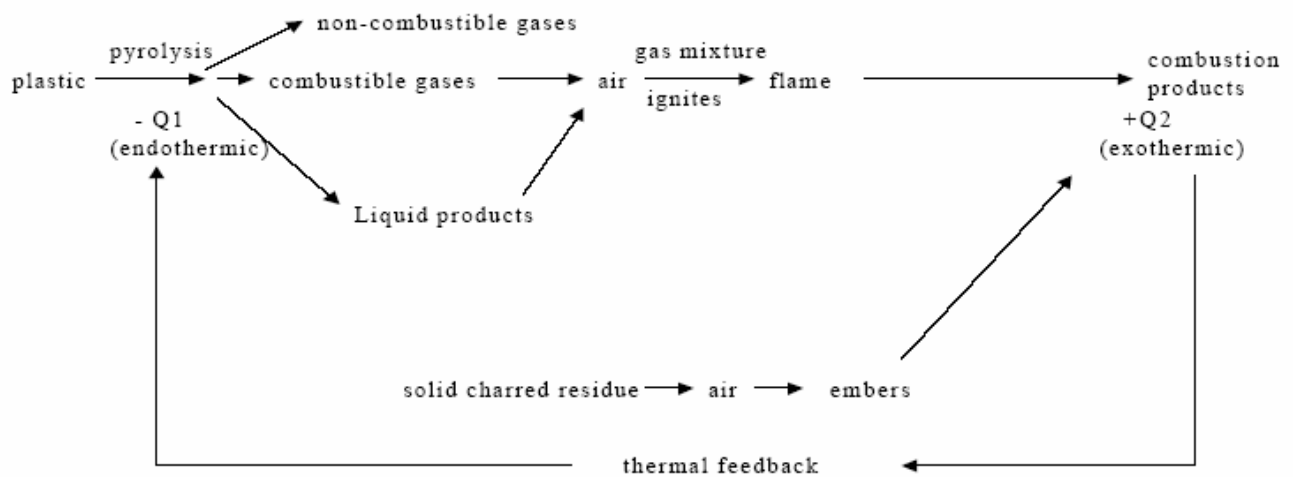


Figure 1: Pyrolysis-Combustion Cycle⁸

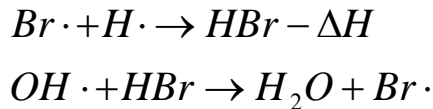
2.0 Flame-Retardant Families

Different substances retard flames in different ways, and have been divided into four major molecular families: halogenated, phosphorus containing, nitrogen containing and inorganic flame-retardants.

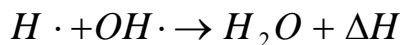
2.1 Halogenated Flame-Retardants

2.1.1 Halogenated Mechanism

Halogenated flame-retardants are chemicals that are added to the material it is protecting, primarily during production, which contain halogen atoms. The halogens primarily used in flame-retardants are bromines and chlorines, with a main focus on bromines. Bromines are used more often in halogenated flame-retardants, because they are less electronegative, less reactive, and have weaker bond strengths than chlorine, which make bromine bonds easier to break apart. When the material combusts, it also combusts the flame-retardant molecule and halogen atoms are released into the vapor phase as free radicals. Once in the vapor phase, the radical halogens bond with the hydrogen and hydroxide radicals present as products of combustion. Once these $H\cdot$ and $OH\cdot$ radicals are halogen bound, they react and form water molecules and diatomic hydrogen as shown below³.



If there is no flame-retardant action, the $H\cdot$ and $OH\cdot$ radicals combine in an exothermic reaction forming water.



By taking these high-energy radicals out of the vapor phase, the energy released is lowered causing temperature to decrease, which reduces the pyrolysis reaction rates. With a lowered amount of flammable gases entering the combustion reaction, the rate of new material combusted is effectively slowed; therefore, allowing for the fire to be extinguished and/or a safe escape. The five most common brominated flame-retardants are tetrabromobisphenol A, hexabromocyclododecane, decabromodiphenyl ether, octa-bromodiphenyl ether, and penta-bromodiphenyl ether. These brominated flame-retardant are incorporated as additives in polystyrene and epoxy resins².

2.1.2 Pros and Cons of Halogenated Flame-Retardants

As with all chemicals, halogenated flame-retardants have their strengths and weaknesses. Detailed below in Table 1 is a breakdown of the pros and cons of halogenated flame-retardants.

Table 1: Halogenated Flame-Retardant Pros/Cons^{3&9}

| Pros | Cons |
|--|--|
| More compatible with modern manufacturing processes – aromatic molecules can be added to plastics in high temperature conditions | Potentially toxic by forming dioxins, furans, etc. |
| Relatively low cost of production and raw materials | Once released into the environment, compounds are not biodegradable |
| Proper disposal can be used for energy recovery. | Improper disposal of flame-retardant plastics can release toxic compounds (i.e. burning in a landfill) |

2.1.3 Uses of Halogenated Flame-Retardants

Halogenated flame-retardants, especially brominated flame-retardants, are used in a number of consumer products ranging several categories. Table 2 lists common industrial uses for halogenated flame-retardants.

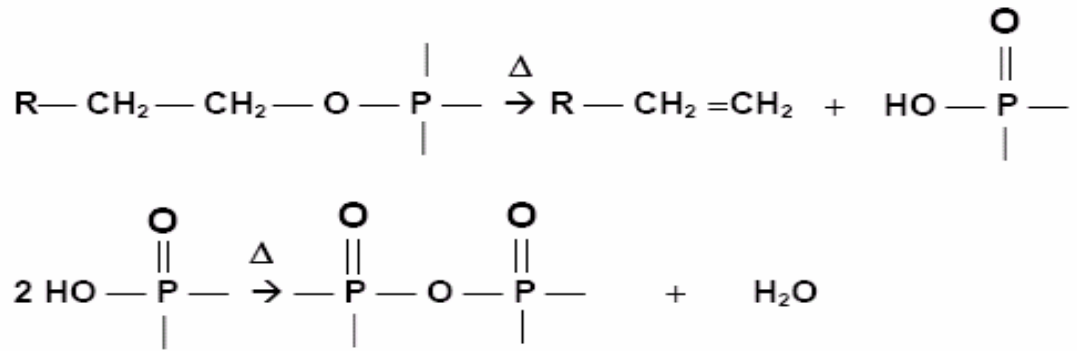
Table 2: Halogenated Flame-Retardant Uses¹⁰

| Categories in Industry |
|--|
| Transportation-circuitry and foam inside cars, trains and planes |
| Building and Construction-in fire resistant doors and safe rooms |
| Electronics and Electrical |
| Textile/Other |

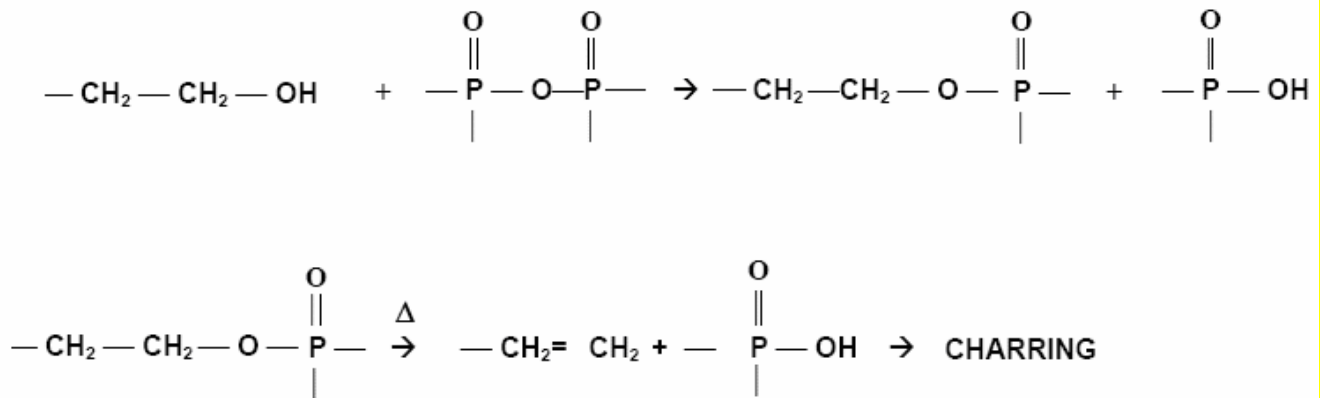
2.2 Phosphorus Containing Flame-Retardants

2.2.1 Phosphorus-Based Flame-Retardants

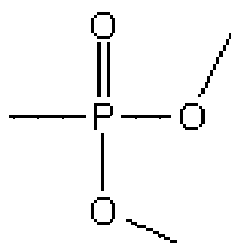
Phosphorus containing flame-retardants act in the solid phase, as opposed to the vapor phase action of halogenated flame-retardants. They are typically mixed in with the material during production. When heated, they react to form a polymeric form of phosphoric acid. This acid coats the material it is protecting and causes the material to “char”. The “char” layer covers the material and interferes with pyrolysis, preventing the plastic from decomposing and releasing combustible vapors. The combustion reaction, and specifically, the pyrolysis step are thereby slowed and the temperature of the material is lowered, which in turn decreases the rate of pyrolysis further³. The detailed mechanism of the basic flame-retardant (using one example) is as follows: First, thermal decomposition leads to the formation of polymeric phosphoric acid¹¹.



Next, the phosphoric acid formed esterifies, dehydrates the oxygen-containing polymer and causes charring³. The polymer is shown in the first line as propanol. Also, the chemical structure of the char is not fully understood, which is why it is stated as simply “char”. What is known is that it is comprised mainly of hydrogen and carbon. The structure of char also varies depending on the structure of the polymer it is created from. Foamy char is usually a better insulator than hard, brittle char.



Dimethyl-methyl-phosphonate (shown below) is a common phosphorus based flame-retardant. It works in the same manner as described above, and is shown below. The R chains that were described above are simply methyl groups.



Dimethyl-methyl-phosphonate²⁰

2.2.2 Pros and Cons of Phosphorus Containing Flame-Retardants

Just like halogenated flame-retardants, there are upsides and downsides to phosphorus containing flame-retardants. A detailed breakdown of the pros and cons is shown below in Table 3.

Table 3: Phosphorus Flame-Retardant Pros/Cons³

| Pros | Cons |
|---|---|
| Efficient FR Performance | Higher price/kg than Halogenated |
| Needed Dosage Lower than Halogenated FRs | Have Limited Industrial Uses because of Mechanism |
| Does Not Produce Toxic Smoke | |
| Does Not Produce Toxic Dioxins and Furans-described in more detail in Section 3.2 | |

2.2.3 Uses of Phosphorus Containing Flame-Retardants

Phosphorus containing flame-retardants are used in a number of products, similar to the other flame-retardant families. However, phosphorus containing flame-retardants are used in only a few industries because of their mechanism (Table 4). A charring film is undesired in several industry, thus preventing phosphorus containing flame-retardants from being used, such as flame-resistant pajamas.

Table 4: Phosphorus Flame-Retardant Uses³

| Categories in Industry |
|------------------------|
| Plasticizers |
| Plastics |
| Polyurethane Foam |

2.3 Nitrogen Containing Flame-Retardants

2.3.1 Nitrogen Containing Mechanism

While halogenated and phosphorus containing flame-retardants have well understood mechanisms, the nitrogen containing flame-retardant's mechanism is not understood fully. What researchers do know, however, is that it releases nitrogen gas into the atmosphere. Also, in some cases, melamine "is transformed into cross-linked structures which promote char formation."³ This inert gas lowers the concentration of combustible gas which slows the reaction. Nitrogen containing flame-retardants are often combined with phosphorus containing flame-retardants to increase the overall flame-retardant efficiency³. Melamine, $C_3H_6N_6$, a common nitrogen flame-retardant

works in a variety of ways to hinder the combustion cycle. First of all, since it has a heat of combustion that is 40% of hydrocarbons, it not a good fuel. Also, it produces nitrogen gas which dilutes the flammable flames. It has also be shown to contribute to the production of the char layer.

2.3.2 Pros and Cons of Nitrogen Containing Flame-Retardants

Similar to the halogenated and phosphorus containing flame-retardants, nitrogen containing flame-retardants have advantages and disadvantages as well. Table 5 outlines the pros and cons of the nitrogen containing flame-retardants.

Table 5: Nitrogen Flame-Retardant Pros/Cons³

| Pros | Cons |
|---------------------------------|--|
| Can partially replace other FRs | Must be used in high concentration |
| | Usually needs to be with another FR |
| | More experimentation needed to determine if it will work, because the mechanisms are not well understood |

2.3.3 Uses of Nitrogen Containing Flame-Retardants

Just as with halogenated and phosphorus containing flame-retardants, nitrogen containing flame-retardants are used in a number of products. The categories that nitrogen containing flame-retardants have been specialized to are listed below in Table 6.

Table 6: Nitrogen Flame-Retardant Uses³

| Categories in Industry |
|-------------------------------|
| Foams |
| Nylons |
| Polymers |

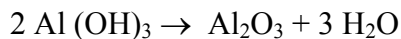
2.4 Inorganic Flame-Retardants

2.4.1 Inorganic Mechanism

Inorganic flame-retardants do not evaporate in the presence of heat, like organic flame-retardants. Instead, inorganic flame-retardants undergo decomposition reactions, which release water or non-flammable gases into the system where they dilute the mixture of flammable gases. These decomposition reactions are endothermic; therefore, taking energy away from the fire. Often, a non-flammable, resistant layer, similar to char, forms on the substrate shielding the surface from the effects of oxygen and heat. This layer interferes with pyrolysis and hinders the combustion reaction³.

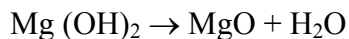
Inorganic flame-retardants are usually used in combination with other types of flame-retardants. Inorganic compounds have relatively low efficiencies and therefore must be used in large concentrations without modifying the material's performance properties. Types of inorganic flame-retardants include aluminum hydroxide, magnesium hydroxide, boron containing compounds, antimony oxides, and inorganic phosphorus compounds. The most common inorganic flame-retardants are aluminum hydroxide and magnesium hydroxide.

Aluminum hydroxide is the most widely used flame-retardant. It is low in cost and incorporates easily into plastics. Aluminum hydroxide breaks down into aluminum oxide and water at a temperature of about 200°C. The decomposition reaction is:



The endothermic breakdown of aluminum hydroxide cools the material (usually a polymer) preventing the pyrolysis combustion cycle from occurring. The aluminum oxide that forms on the surface acts as an insulating protective layer. It is used in large quantities in PVC, wires, cables, and thermo sets⁸.

The second most common inorganic flame-retardant, magnesium hydroxide, acts in the same way as aluminum hydroxide. It also undergoes a decomposition reaction; however, it initially starts to break down at a higher temperature of 300°C. Because of the high temperature, the magnesium hydroxide is useful in plastics that are manufactured at relatively high temperatures. However, extremely large concentrations of magnesium hydroxide are needed for effective flame retardancy, which can affect the properties of the plastic material. The decomposition of magnesium hydroxide is



Magnesium hydroxide is used in wire and cable applications, polypropylene, and polyamides⁸.

2.4.2 Pros and Cons of Inorganic Flame-Retardants

Similar to the other flame-retardant families, inorganic flame-retardants have advantages and disadvantages as well. Table 7 shows the pros and cons.

Table 7: Inorganic Flame-Retardant Pros/Cons³

| Pros | Cons |
|----------------------------------|-----------------------------|
| Low Cost | Large Concentrations Needed |
| Incorporate Easily into Plastics | |

2.4.3 Uses of Inorganic Flame-Retardants

Just as with all flame-retardants, inorganic flame-retardants can be used in a number of products. Inorganic flame-retardants are primarily located in the relatively selective categories listed below in Table 8.

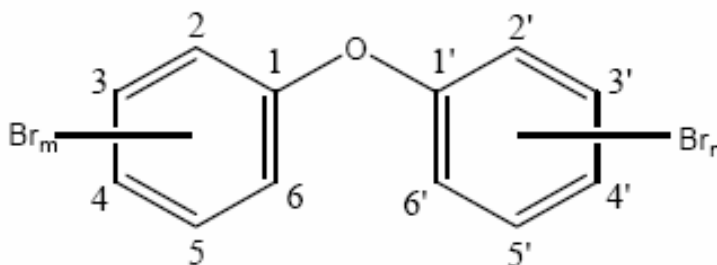
Table 8: Inorganic Flame-Retardant Uses³

| Categories in Industry |
|-------------------------------|
| PVC |
| Wires |
| Propylene |

3 Problem Statement

3.1 Banned Chemicals

Great Lakes Chemical recently announced that it was voluntarily phasing out the production of two polybrominated diphenyl ether flame-retardents: penta-bromodiphenyl ether and octa-bromodiphenyl ether. The generic form of the chemicals is shown in Figure 2.



Where $m + n = 5$ for penta, $=8$ for octa.

Figure 2: Generic Polybrominated Diphenyl Ether¹²

The phase out is essentially preemptive, as the two chemicals will be banned in California, effective by 2008 and in Europe as of next year. While it is a preemptive move, it is also an early phase-out in the US because Great Lakes Chemical is the only domestic producer of these two chemicals¹³. The chemicals are being banned because of toxic traces found in the environment and in humans. The toxic hazards are explained and outlined in greater detail in the next section. These two chemicals are a major part of the brominated flame-retardant market, and because of their absence, there will be a large void to fill. While Great Lakes Chemical believes that it

has a comparable replacement lined up, KSMH's job was to create a more successful replacement for the penta- and octa-bromodiphenyl ethers that are being phased out.

3.2 Environmental Concerns

When brominated flame-retardants, especially octa-bromodiphenyl ether and penta-bromodiphenyl ether, are ignited during the combustion cycle, traces of toxins are present in the soot. However, toxins have not been detected in the fire's gases and no deaths have been documented to date. The toxins found in the soot are known as dioxins and furans, which are some of the most toxic chemicals⁸. Structures of dioxins and furans are presented in Figure 3.

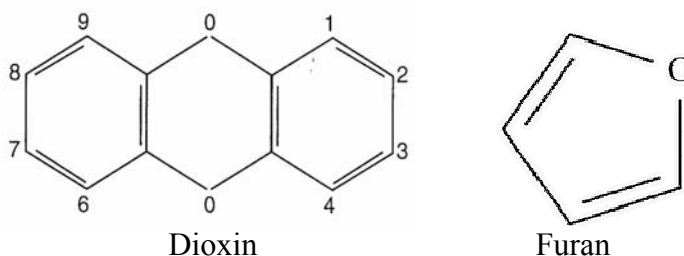


Figure 3: Structures of Dioxin and Furan^{14&15}

Dioxins are produced as an unintentional by-product of many industrial processes involving halogens. They are formed by burning halogen-based chemical compounds with hydrocarbons. The EPA has stated that dioxins present a cancer hazard to people, with strong indication towards breast cancer. Dioxins cause severe reproductive and developmental problems. They also damage the immune system and interfere with hormonal systems. Dioxin has been linked to birth defects, decreased fertility, reduced sperm count, and lowered testosterone levels¹⁶.

In turn, furan is a volatile liquid used in the production of nylon and traces of furan has been detected in some foods¹⁷. Furans have dioxin-like effects. It causes cancer in animals, which begs the question: will furans eventually cause cancer in humans through long-term exposure¹⁷?

Exposure to both toxins has been linked to attacks on the nervous system during the first trimester, a critical phase of neonatal brain development, which results in mild impairments in spontaneous motor behavior, learning, and memory. The toxins also attack the thyroid. This attack on the thyroid is a cause for concern, due to the thyroid's critical role in the development of the central nervous system. Unfortunately, a limited amount of information is available on the effects of these toxins on the rest of the human body¹⁷.

4.0 Chemical Alternatives

The potential replacement product should preferably be an original molecule, not currently used as a flame-retardant, with excellent flame-retardant properties and good commercial potential.

The discovery of dioxin formation as the leading cause for PBDE health concerns suggests a halogenated biphenyl molecule as a replacement. Without the oxygen atom between the phenyl groups, the ability to form a dioxin would be severely hindered. Because of the similar structure to the banned substance and the ability to place up to six halogen atoms into the vapor phase per molecule (as shown below in Figure 4) this was thought of as a promising prospect.

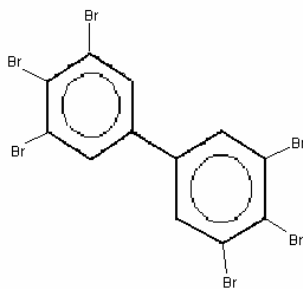


Figure 4: Brominated Biphenyl Molecule¹⁴

However, the likelihood of dioxin formation persists because of the presence of benzene rings. The formation of the dioxin could take place between two biphenyl molecules with available bonding sites due to the vacated bromines. The mechanism of such a formation would undoubtedly be very complicated, requiring oxygen atoms to bond in between the two-phenyl groups.

As a result, it was decided to exclude aromatic molecules from the search so that dioxin formation was no longer a possibility. Since this excludes all known alternatives, molecular discovery was attempted. Molecular simulation was initially restricted to pure hydrocarbons, aromatic compounds, alcohols, amides, and halogen species due to available group contribution data. The properties of the phosphate group were later calculated to allow simulation of a phosphorous-based molecule. Further research showed that the combustion of any halogenated hydrocarbon could produce a dioxin or furan. Our search was therefore restricted to phosphorous-based flame-retardants.

4.1 Molecular Discovery

4.1.1 Background

Molecular discovery refers to a wide range of computer modeling techniques varying from very simple spreadsheets to sophisticated graphically aided software. These techniques enable researchers to predict the collective properties of theoretical molecules and even molecular assemblies under specified external conditions. Simulation software that includes graphical displays can be used to study bulk phase phenomena on a molecular level. All of the simulation techniques at their most fundamental level solve a series of statistical equations based on intra- and inter-molecular interactions¹⁸. There are equations for spatial considerations; which yield accurate molecular stability and volume predictions. There are other equations that predict bond energy and enthalpies of formation, fusion, and vaporization. Molecular

simulation is the most widely accepted technique available for predicting collective properties from atomic or group contributions.

4.1.2 Group Contribution Properties

Through research it was determined that the thermodynamic properties important to flame-retardant performance included vapor pressure and the enthalpies of vaporization and fusion. *Perry's Handbook* referred to a method for using group contributions to calculate critical constants¹⁹. According to *Perry's Handbook*, the Lydersen method is the most accurate method for predicting the critical constants of non-hydrocarbon organic molecules. Because our final product would have to contain some non-hydrocarbon elements to be successful, this method was considered the most promising. The Lydersen method involves mathematical functions for each critical constant, which are dependent on tabulated values for each molecular group in the compound. The equations used in the Lydersen method are listed in Appendix A. The molecular group contributions were differentiated by atoms involved, types of bonds, and aromatic substitution. The available groups were primarily hydrocarbons; with a few halogens and amide groups tabulated also.

For the calculation of the normal boiling point, Stein and Brown's method was used as described in Boethling and Mackay's *Handbook of Property Estimation Methods*²⁵. Stein and Brown's method was used because it covers the widest base of functional group contributions. Other methods are restricted to molecules containing only Carbon, Hydrogen and Oxygen for example. The method is considered accurate

within 4.3% once the temperature correction equations are used²⁵. The equations and method are further detailed in Appendix A.

An excel spreadsheet was set up based on these available groups that calculated the thermodynamic properties of a molecule after the quantities of each group was specified by the user. This spreadsheet was the centerpiece of our molecular discovery effort. Our simulator was tuned for accuracy using the examples in *Perry's Handbook* until computed results matched given experimental values. The available group contribution values for the Lydersen method were entered into the spreadsheet¹⁹ as well as the group contributions for Stein and Brown's calculations. As mentioned above, molecular simulation was initially restricted to pure hydrocarbons, aromatic compounds, alcohols, amides, and halogen species. This presented a fundamental problem when KSMH's focus shifted from designing a halogenated, vapor phase acting flame-retardant to a molecule based on phosphorous. This decision was made after industry research indicated that the production capacity required for a phosphorous flame-retardant plant would be smaller than that for a halogen based compound. Additionally, the amount of flame-retardant that must be added to the plastic is significantly less than for other flame-retardant families. With consideration of the potential environmental and health risks, a phosphorous-based compound was deemed the best alternative. If KSMH were to successfully compute critical constants for our desired product we would need the Lydersen and Stein & Brown contribution values for the phosphate group shown in Figure 5.

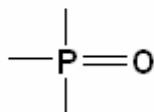


Figure 5: Phosphate Group

The contributions for this group were obtained using phosphoric acid (H_3PO_4), as a reference material for property simulation. Using Excel's solver and goal-seeking utilities, KSMH was able to determine the phosphate group contributions to both equation sets, which enabled us to simulate a phosphorous-based flame-retardant molecule and its properties.

4.1.3 Simulation Procedure

The solver add-in was configured to maximize the enthalpy of fusion by varying the quantities of each group. Original constraints included:

- Quantities must be positive integers
- Normal Boiling Point must be greater than 513 Kelvin
- Quantity of phosphate group greater than or equal to one
- Quantity of -O- groups must be greater than or equal to three times the quantity of phosphate groups. (This facilitates polymeric phosphoric acid formation)

The resulting molecules generated by Excel's solver choosing just the number of groups in it, could not balance the number of available bonding sites and the number of bonding sites used. As a result, molecules generated could have chemical

structures with free electron pairs – virtually assuring unwanted reactivity. Further, the group contribution method does not account for connectivity, which necessitates a known molecular configuration before the simulator is run. Another issue is symmetry around the central phosphate group. As explained in the phosphorous containing flame-retardant Section 2.2, the charring action is caused by a reaction between the plastic surface and a polymeric form of phosphoric acid. This phosphoric acid chain forms from a phosphate group monomer. So in order for phosphorous-based flame-retardants to perform well, it was reasoned that the three chains attached to the phosphate group must be equally ‘motivated’ to leave the phosphate to induce polymer formation.

One answer to this is to use identical chains at each bonding site, creating symmetry around the central phosphate group. Even if these extra considerations are used, the group contribution method is still able to produce results that do not constitute a valid molecule. Theoretically, discovery of flame-retardant molecule using group contribution method alone is not possible.

Therefore, the decision was made to use the ‘simulator’ to generate flame-retardant performance properties of known molecules containing a phosphate group. Using the *NIST Chemistry Web Book* to generate a list of phosphate containing molecules, we were able to test different molecules for potential flame retardancy²⁰. Preliminary exclusions were made based on the presence of an aromatic ring or a transition metal (groups 3-12). Phenyl groups were excluded based on ability to form dioxins. Metals

were excluded based on available group contribution data as well as concern over the oxidized products of combustion. After these initial screenings reduced the field from 197 molecules to 19, the group quantities were user-fed into the simulator and another round of eliminations were made based on the normal boiling point constraint. There were four molecules that remained after these eliminations. The vapor pressure of each molecule was computed at the polystyrene plastic melting point of 513 Kelvin to determine the molecule's ease of volatilizing during combustion. Polystyrene was used as a reference material based on its extensive use in the electronic industry. The spreadsheet was set up to allow a user-input desired temperature based on the melting point of each plastic. After calculating the vapor pressure according to the equations in Appendix A, the molecules were then ranked in increasing order according to this vapor pressure, as shown in Table 9 below.

Table 9: Rankings of Molecules Made

| Rank | Molecule | T _c | P _c | V _c | Vapor P @ 513K | |
|------|----------------------------------|----------------|-----------------|-----------------------------------|-----------------------|-----------------------|
| | | (K) eq 2-3 | (MPa) eq 2-7 | (m ³ /kmol) Eq 2-14 | (MPa) (± 10 - 30%) | (atm) |
| 1 | Tri-n-Butyl Phosphate | 800.5 | 1.379 | 0.959 | 0.0019 | 0.0187 |
| 2 | Tri-ethyl Phosphate | 804.8 | 1.969 | 0.629 | 0.1996 | 1.970 |
| 3 | Tri-Isopropyl Ester | 771.1 | 1.667 | 0.782 | 0.2556 | 2.523 |
| ** | Tris(2,3dibromopropyl) phosphate | 613.1 | 1.579 | 0.782 | 6.05 x10 ⁶ | 5.971x10 ⁷ |

Although it ranked last according the vapor pressure, the molecule, Tris(2,3-dibromopropyl) Phosphate showed very good potential as a flame-retardant based on its structure (Figure 6).

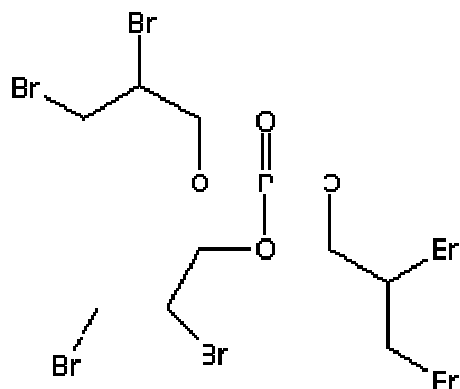


Figure 6: Firemaster t23p™²⁰

If a thermal decomposition occurs before the plastic melting point is reached, then the terminal bromine atoms would have the ability to be radicalized into the vapor phase upon combustion. The high number of Bromine atoms per molecule would make this an effective vapor-phase acting flame-retardant without all of the environmental concerns of the banned molecules. The remaining phosphate core would also have the ability to char the plastic surface. Unfortunately, we discovered that this molecule is already being sold as “Firemaster t23p” by Great Lakes Chemicals. The molecule with the lowest vapor pressure at the plastic melting point, Tri-n-Butyl Phosphate displays a vapor pressure low enough to remain on the plastic surface during combustion. This molecule was chosen as the replacement flame-retardant and is presented in Figure 7.

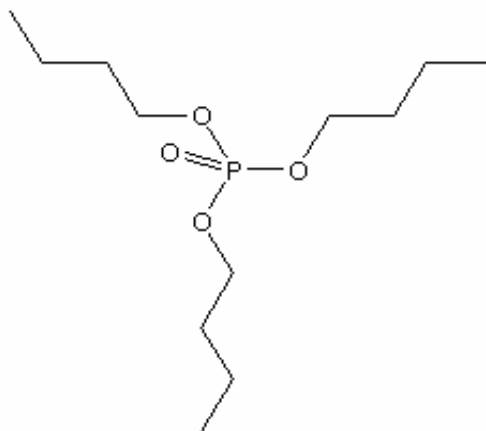


Figure 7: Tri-n-Butyl Phosphate²⁰

Additional details about the molecule, including reaction and mechanism of synthesis are described in Section 5.0.

4.1.4 Additional Considerations

In order for the molecular discovery process to be more effective, solution software more powerful than Excel should be sought after and used. Without it, KSMH is restricted to computing properties of known molecules or guessing a boiling point before the molecule is even simulated. It should be noted that while property prediction indicates strong flame-retardant performance, laboratory testing is necessary before production is considered. The testing for our molecule is outlined in Section 5.4 and in the Appendix B.

5.0 Properties of Tri-n-Butyl Phosphate

The molecule chosen is called Tri-n-Butyl Phosphate, renamed Flame-O 1000™ by KSMH. A molecular diagram is provided below in Figure 8.

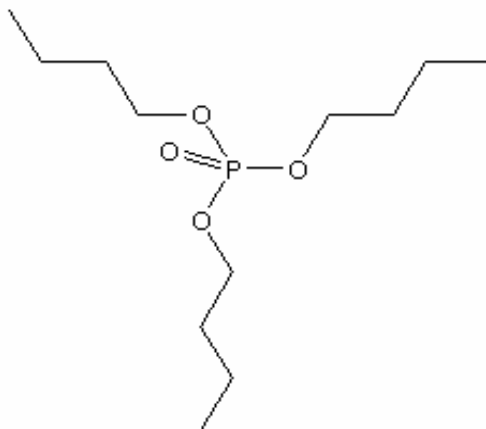


Figure 8: Flame-O 1000™

KSMH believes that Flame-O 1000™ will be a good flame-retardant because it meets the criteria discussed in molecular discovery. Flame-O 1000™ has a low vapor pressure at high temperatures, along with a high heat of combustion. A detailed breakdown of compound properties is listed below in Table 10. The molecule is also lacking aromatic benzene rings, which eliminates the possibility of the formation of dioxins; however a small possibility is still there for the creation of furans.

Table 10: Flame-O 1000™ Property List

| Property | Value |
|------------------------|----------------------------|
| Critical Temperature | 800 K |
| Critical Pressure | 1.38 Mpa |
| Critical Volume | 0.943 m ³ /kmol |
| Vapor Pressure @ 240°C | 0.0187 atm; 0.00191 MPA |

5.1 Synthesis Path

A number of synthesis reactions were examined when determining the synthesis needed. It was apparent that a phosphoric acid derivative would be needed to create the core of the molecule. Also, there would need to be several alkane chains after the oxygen molecules. It was the feeling of KSMH that a simple reaction would be best, with multiple steps causing waste and a lower conversion. A more detailed approach could be used when determining these other possible reactions. It was proposed at first to have phosphoric acid react with 1-bromo butane. It was thought that this reaction would not be as productive as the final proposed reaction, however. The reaction synthesis was narrowed down to a reaction between n-butanol and phosphoryl chloride and one between 1-bromobutane and phosphoric acid, shown below.

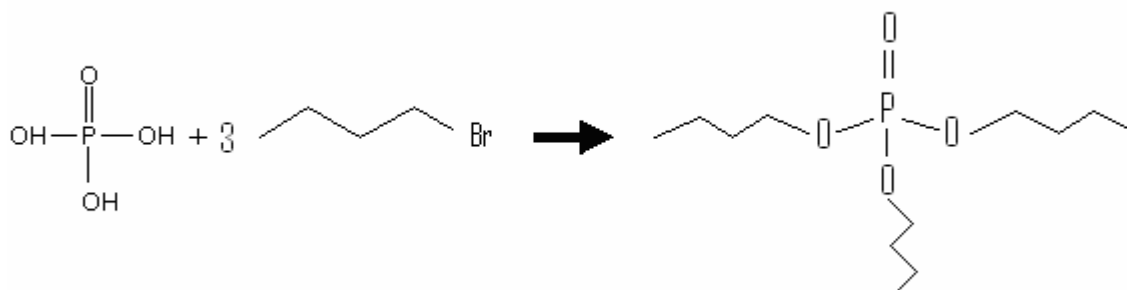


Figure 9: Phosphoric Acid and 1-Bromobutane Reaction Synthesis

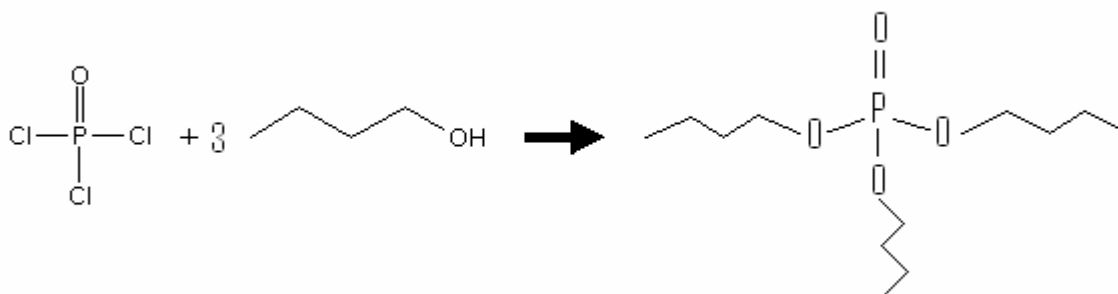


Figure 10: Phosphoryl Chloride and n-Butanol Reaction Synthesis

The raw materials for 1-bromobutane and phosphoric acid cost less, however the specifics of the reaction make it less economical and efficient. The reaction between 1-bromobutane and phosphoric acid will require a substantial amount of heat, and will be slow and inefficient. The first reason why the reaction between involving n-butanol is the desired synthesis is because of the reaction occurs at room temperature, or slightly above, and occurs very quickly due to the high reactivity of phosphoryl chloride. This reaction also has a high efficiency, also due to the high reactivity of phosphoryl chloride. It is believed that this is a valid reaction for a number of reasons. First of all, the reaction could occur through an addition reaction with the Cls as the leaving groups. Halogens are good leaving groups because they have high polarity and the hydrogen on the alcohol is a good initiator because it is a highly nucleophilic Lewis base²². In the reaction, the nucleophilic alcohol (initiator) attacks the central phosphate, which releases the chlorine (leaving group).

The proposed reaction synthesis for the formation of Flame-O 1000™ is provided below in Figure 11. This synthesis takes phosphoryl chloride and n-butanol in

combination to create Flame-O 1000™. The reaction synthesis is known to work and be the best reaction to create tri-n-butyl phosphate, however the kinetic specifics are not known. Because of this, a detailed testing is suggested to determine values such as percent yield and activation energy. Due to time constraints, these experiments were not performed, however a detailed experimental plan is provided in Appendix B 12.1.

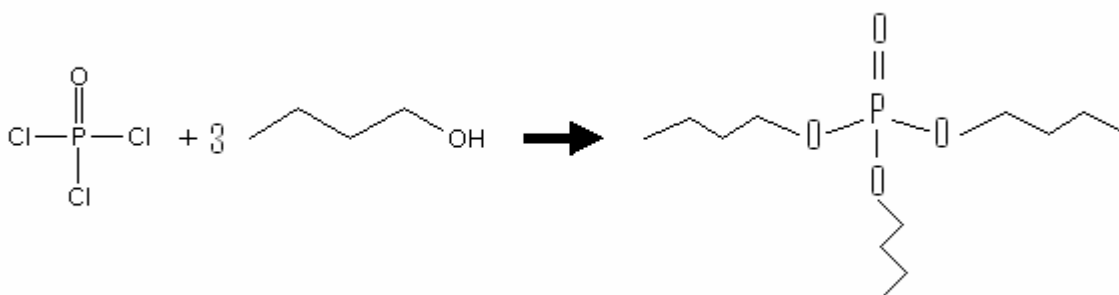


Figure 11: Flame-O 1000™ Reaction Synthesis

5.2 Raw Materials

The n-butanol is a chemical that is readily available and can be purchased from a number of sources. The phosphoryl chloride is less common, and is thus the more expensive of the two raw materials. A price comparison has been performed on the two reactions, and the price of the 1-bromobutane reaction was cheaper, however the operating costs make it more expensive.

5.3 Proportions of Product

For production and marketing purposes, it will be necessary to know to the weight percents required of the product as an additive or coating that will be required for the product to work efficiently. These experiments were not performed, however a detailed experimental plan is provided in Appendix B 12.2 and 12.3.

5.4 Qualitative Testing

The effectiveness of our product was tested in a qualitative manor in order to physically determine its potential as a flame retardant. A detailed experimental plan is provided in Appendix B 12.4.0. When testing Flame-O 1000TM, five runs were performed. The first three runs involved all three samples, untreated polypropylene, treated polypropylene (Flame-O 1000TM as an additive) and untreated polypropylene coated with the flame retardant. The first of these runs was used as a trial, to adjust the testing procedures so that general results could be determined. The results from our testing are provided below in Table 11. It should be noted that the samples all had the same weight (10g), the exact shape varied from sample to sample. An effort to get each sample into similar shapes was made, however it was not possible to get them precisely the same.

Table 11: Flame-O 1000™ Qualitative Testing

| Run # | | Untreated | Treated | Coated |
|--------------|-----------------------|------------------|----------------|---------------|
| 2 | Time to Start Burning | 11.5 sec | 14.6 sec | 14.5 sec |
| | (Go Out)/Be consumed | 30.9 sec | (75.5 sec) | 43.2 sec |
| 3 | Time to Start Burning | 15.0 sec | 21.6 sec | 25.0 sec |
| | (Go Out)/Be consumed | 30.5 sec | (67.7 sec) | 53.6 sec |
| 4 | Time to Start Burning | -- | 21.4 sec | 23.4 sec |
| | Be consumed | -- | 112.8 sec | 78.7 sec |

From our experimentation, it was obvious that the treated and coated samples took much longer, nearly twice as long in one run, to catch fire. Between the treated and the coated samples, the data shows that the treated sample caught fire first, although there was not a substantial time difference between the two. It is assumed that with a larger sample size, the time difference would be more significant. After the samples catch fire, it takes a noticeably longer time for the entire treated sample to become entirely engulfed in flames and consumed. While testing, the samples would frequently catch fire and then drop off the screen down onto the aluminum foil once the samples were liquid or small enough to fit between the cracks in the screen. It can be seen in Figure 12 how the samples produced a char on the surface after the flames had gone out.



Figure 12: Charring

In several of the runs, the flames would consume the sample until the entire untreated sample fell between the cracks, while the other two samples would remain after the flames finally went out. This is shown below in Figure 13, where the far left is the untreated plastic sample, the middle top is the treated sample, and the far left is the coated sample.



Figure 13: Samples After Tests

While the times to catch fire and be consumed were much longer for the treated samples, there was a greater amount of smoke produced during burning compared to the untreated polypropylene. The coated sample produced an even greater amount of smoke during the first few seconds after catching fire. It is suspected that this is the burning of Flame-O 1000TM and then after that it was simply the plastic burning. The treated samples had an increased smoke production, but it was substantially less than the coated, and only slightly more than the untreated plastic sample.

While the time differences do not seem to be a great deal, only 15 or 30 seconds more, it should be noted that the samples were heated by direct exposure to an open flame and the base plastic has a rather low melting temperature (160C). If a plastic with a higher melting point was used, it can be reasoned that the time differences would have been different. The significance of the time differences becomes clearer when the sample size is taken into consideration. As the weight of the plastic used in a product increases, the time difference between a treated and untreated sample would grow significantly. Also, under working conditions, the exposure to such a high temperature flame for sustained periods of time would be minimal. From the testing, it has been definitively been shown that the treated plastic material is more resistant to both catching fire and sustaining flames than its untreated counterpart.

It can be determined that our product does indeed retard fire. What cannot be determined from our limited testing is how it compares to other flame-retardants that already exist in the market. The testing set-up had limitations that prevented us from reproducing the 94 HB Horizontal Burn Test, described in Appendix B12.5.2.2. Assuming that our set-up had a close approximation to the set-up of the 94 HB Horizontal Burn Test, then Flame-O 1000TM would meet the requirement for achieving certification, namely the flame extinguished in less than 5 minutes. When looking at the 94V Vertical Burning Test criteria, it appears that our product extinguishes in appropriate ranges, often between 30 and 50 seconds. Flame-O 1000TM does produce drips, however, so it is limited in its possible rankings.

A qualitative analysis was performed; however there are still several more tests that should be performed on Flame-O 1000™ to assess the exact quantitative effectiveness before it is entered into the market. These testing methods are described with set-ups in Appendix B 12.5.0.

5.5 Happiness Function

In order to evaluate the expected demand for our product, it must be compared to other flame-retardants without regard to price. Demand for our product when compared to available flame-retardants without regard to pricing can be considered a function of buyer happiness. The “happiness function” output, (β) quantifies the deviation from an established threshold value for different flame-retardant properties. These property deviations are weighted by relevance to consumer happiness and the sums are compared for competing molecules. The happiness function developed for the flame-retardant market is shown below.

$$\sum W_i \cdot (Y_i - X_i) = \beta$$

Table 12: Happiness Function

| | W_i | Threshold (Y_i) | Product (X_i) | Banned Molecule (X_i) |
|--------------------------|-------|------------------------|----------------------|------------------------------|
| Speed of FR action | .4 | 120 s | 75.5 s | -- |
| Effective Weight % | .25 | 30% | 20% | 25-30% ² |
| Ease of Application | .25 | 5 | 3 | 3 |
| Environmental Effects | .1 | 5 | 3 | 8 |

As the table shows, the speed of flame-retardant action is the most important factor in selecting between equally priced flame-retardants. This speed is identified by the time required for the flame-retardant to work on the material. In testing, this time was observed as the time for flames to be extinguished. The 120-second threshold value was obtained from the ASTM standards. The banned molecule speed of FR action could not be obtained, however, when comparing Flame-O 1000™ to another available flame-retardant, testing should be done to attain this value.

Of equal importance to buyer happiness are the ease of application and the effective weight percentage. The effective weight percentage is important even if cost is not an issue. A higher weight percentage causes further deviations from designed material performance, such as flexibility, transparency, etc. The threshold value of 25% is based on these material performance concerns. Industry research indicates that the phosphorous-based flame-retardants have the lowest required weight percentage. The banned molecule has been documented as being up to 30% of the final material weight. The weight percentage used in our experiments, 20%, showed effective flame-retardant action. We recommend further testing to find the least effective weight percentage to further increase buyer happiness.

Ease of application and environmental effects are non-quantifiable criteria that must be based on a numerical scale for comparison. A 1 to 10 scale is used for each with the threshold value being established at the mid-range (5). For both scales, lower numbers are considered as increasing buyer happiness.

Ease of application is important to buyer happiness since more difficult applications would imply higher operating costs such as utility or labor. The threshold value corresponds to a more complex application than surface coating, with limited utility required for the flame-retardant addition. Our flame-retardant must be added after plastic pellet formation and before molding. It received a value of 3 because it would not need any additional utility, as it would be added when plastic is melted. Similarly, the banned diphenyl ethers were applied to foams and plastics as an internal additive during molding.

Environmental effects were the least important factor in determining buyer happiness since the toxicity of materials is monitored and regulated by the EPA. These effects are considered only in the sense that a material with very few environmental effects is beneficial for product image and long-term usage. Flame-retardants with suspected environmental hazards have a greater potential to be banned. Our flame-retardant was given 3 out of 10 based on current research. Tri-n-butyl phosphate shows no evidence of the bioaccumulation or developmental interference exhibited by the banned poly-brominated diphenyl ethers.

This happiness function should be used as an evaluation tool when comparing our flame-retardant to other molecules. The computed buyer happiness (β) of 21 can be compared to the β value computed from testing another flame-retardant. From a

research and design standpoint, the happiness function also provides a goal for product improvement based on the β values of other flame-retardants.

6.0 The Market

6.1 World Market

The flame-retardant market is large and spread into many different products. Flame-retardants are a part of plastics, textiles, foams, electronic housings, and many other products. As of 2002, the global market broken down by family was 24% phosphorus, 27% inorganic, 6% chlorine, 39% bromine and 4% other, as shown below in Figure 14¹⁰. The global production of flame-retardants is 2.2 billion pounds for a value of \$2.1 billion.

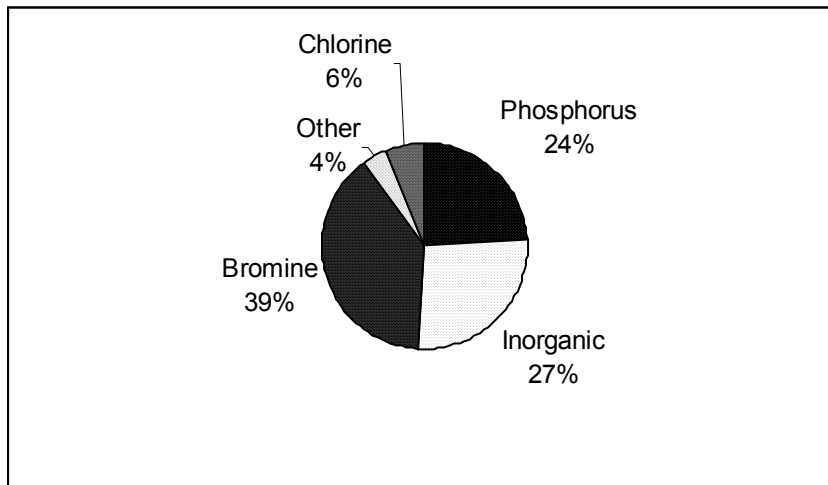


Figure 14: Global Market Breakdown¹⁰

6.2 US Market

The United States market makes up over 50% of the global market. The United States production is 1.1 billion pounds for a total of \$1.3 billion²³. The US breakdown is very similar in-group distribution to the global breakdown.

6.3 Brominated Flame-Retardant Market

With a major contributor to the brominated flame-retardant market being phased out, there will be a large void to fill. The brominated flame-retardant market is divided into transport, building and construction, textile/other, and electrical & electronics. The percentage breakdown is provided in Figure 15¹⁰. When examining the market statistics in Figure 15, it is noticeable that brominated flame-retardants account for \$819 million, globally, and \$507 million in the US. Because of this, our product has a large market to break into and fill the gap left from the phasing out of polybrominated diphenyl ethers.

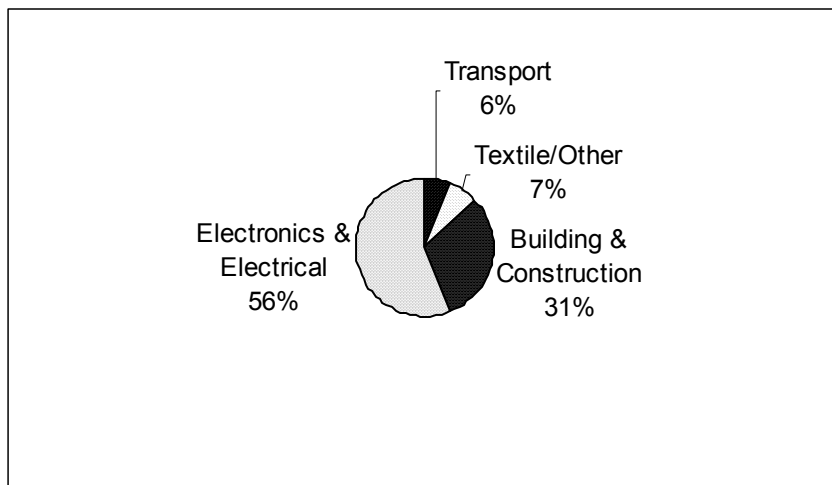


Figure 15: Brominated Flame-Retardant Market

6.3.1 Brominated Sellers

The majority of brominated flame-retardants are sold by only a few companies. There are several small companies, but just a few major corporations sell the largest portions. These corporations are listed below in Table 13.

Table 13: Brominated Flame-Retardant Sellers

| |
|---|
| Brominated Flame-Retardant Sellers |
| Great Lakes Chemical |
| Albemarle |
| Dead Sea Bromine Group |

6.4 Phosphorus Containing Flame-Retardant Market

While our product will be filling a gap in the brominated flame-retardant market, it will also be a superior alternative to all the phosphorus flame-retardants already in the market. By breaching the phosphorus containing market, our product will be venturing into a \$504 million global market, and \$312 million United States market.

6.4.1 Phosphorus Sellers

Like brominated flame-retardants, the majority of phosphorus-based flame-retardants are sold by only a few companies. These corporations are listed below in Table 14.

Table 14: Phosphorus Containing Flame-Retardant Sellers

| |
|--|
| Phosphorus Containing Flame-Retardant Sellers |
| Great Lakes Chemical |
| Albemarle |
| Dow Chemicals |

6.5 Market Status

In the United States, projections show that the demands for flame-retardants will increase by 3.6% per year for production from 1.1 billion pounds in 2003. The value is expected to grow 5.9% annually²³. With a production in pounds growing 3.6% and the monetary value increasing 5.9%, it is shown that the worth of the flame-retardants should increase. This increase is due to higher standards and higher use in industry. This value is expected to grow because specialty flame-retardants should increase their share of the market²³. It is our feeling that these predictions are realistic, based on the reasoning that flame-retardants are becoming more specialized, and with an increased specialization comes a higher cost. Also, with a more specialized market, more products will be produced than in previous years, leaving the market with a higher production.

Along with more specialized flame-retardants, more items are being made from plastics. With the ability to reduce weight by eliminating glass and metal and to lower production costs while improving design and production flexibility, the need for more flame-retardants in specialized plastic flame-retardants will increase as well.

7.0 Business Plan

7.1 Companies Targeted for Technology

Flame-retardant technology is not economically feasible if the company makes only one flame-retardant and does not account for expansion. It will create a profit; however, it could be a large gamble to have a plant and company creating only one product. For these reasons KSMH has compiled a list of companies that we feel would benefit financially by producing Flame-O 1000™. Provided below in Table 15 is the list of these companies. The list is broken into companies already producing flame-retardants, companies that produce plastics, the major consumers of Flame-O 1000™, and companies that produce computers.

Table 15: Target Companies

| Flame-Retardant Producers | Plastic Producers | Computer Producers |
|----------------------------------|--------------------------|---------------------------|
| Great Lakes Chemical | Dow Chemicals | Hewlett-Packard/Compaq |
| Albemarle | ChevronPhilips | Dell |
| Dow Chemicals | BP | IBM |
| Dead Sea Bromine Group | Shell | Apple |

7.2 The Offering

Since Great Lakes Chemical is phasing out penta- and octa-bromodiphenyl ether as a result of the California ban, KSMH has decided to manufacture a flame-retardant that could fill the void in the market. A flame-retardant is a chemical added to combustible materials to render them more resistant to ignition. Our product, Flame-O 1000™, is designed to prevent fires from spreading by forming carbon char over

the material's surface; slowing the combustion cycle and allowing time for either the flame to be extinguished or an escape can be made.

7.2.1 Description

Flame-O 1000TM is a phosphorus containing flame-retardant which was designed to inhibit flames in plastics that encase electronic devices such as computers. A detailed description of our product and phosphorus containing flame-retardant mechanism can be found in Sections 2.2 and 5.0.

7.2.2 Market Status

Flame-O 1000TM is marketed as a flame-retardant for the plastic industry to be used in housing for electronics. The phasing out of penta- and octa-bromodiphenyl ether has created a void in the market. KSMH is seeking to obtain approximately 3.5% of the vacated brominated market, which \$819 million, globally, and \$507 million in the US. This leaves a huge opportunity for KSMH's Flame-O 1000TM to fill the vacancy left in the brominated market as well as a chance to enter into the phosphorus market. Another factor for targeting this market is the increased use of plastics, especially with the ability to reduce weight and lower production costs while improving design and production flexibility. For more information about the market, refer to Section 6.0.

7.2.3 Cost to Produce

The materials needed to produce Flame-O 1000TM are n-butanol and phosphoryl chloride. The necessary amounts and costs of each material are provided below in Table 16.

Table 16: Component Amounts and Cost

| Components | Unit | Amount | Price (\$/kg) | Cost (\$/yr) |
|---------------------|------|-----------|---------------|--------------|
| n-butanol | Kg | 1,540,000 | \$1.39 | \$2,140,000 |
| Phosphoryl Chloride | Kg | 1,070,000 | \$1.47 | \$1,570,000 |
| Total Raw Material | | | | \$3,710,000 |

The quantities listed in Table 16 are for the production of 1,850,000 kg/yr of Flame-O 1000TM. The manufacturing cost per product is calculated to be \$3.37/kg, which does not include packaging costs. This price is found by dividing the Total Production Cost by desired yearly capacity of Flame-O 1000TM. The Total Production Cost was determined with the assumptions of 5 non-salary workers this expansion process.

7.3 Pricing

KSMH plans to offer the flame-retardant at a price lower than the expected price of our competitor in order to obtain as much of the market as possible. The suggested retail price of Flame-O 1000TM is \$10/kg. This price is about 3 times larger than the cost to manufacture. Great Lakes Chemical, our primary competitor, distributes their phosphorus containing flame-retardants at a range of \$9.00/kg to \$13.27/kg.

7.4 Sales

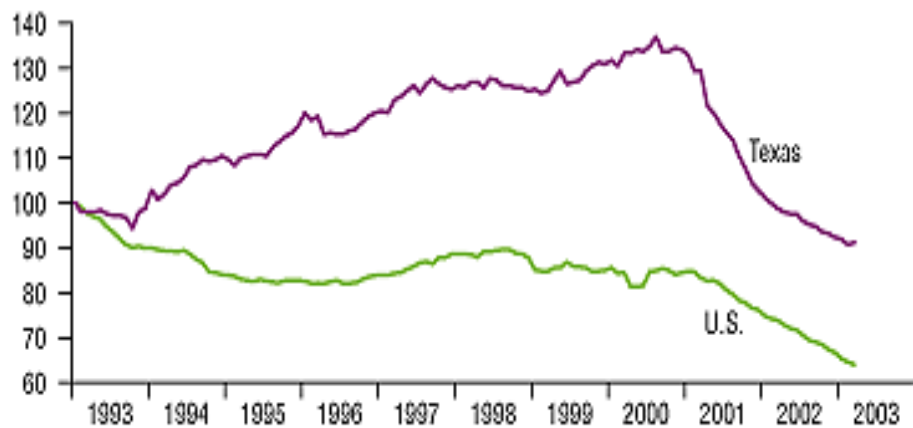
KSMH currently has a staff of 15 personnel who are responsible for the development of our product. They are responsible for promoting Flame-O 1000™ by creating advertisement that will be given to the distributors. Our distributors will focus their efforts on potential industrial buyers of Flame-O 1000™ detailing the key aspects of our product that include non-toxic, low in cost, and market growth. Potential buyers are companies that are producing computers such as Hewlett-Packard/Compaq, Dell, IBM, and Apple. KSMH has decided to focus our efforts on computer companies since computers are encased in plastic. Also, the costs of computers are becoming cheaper, because the demand for computers is a necessity causing the computer market to continue growing. A major selling point for Flame-O 1000™ is that it is non-toxic, unlike the two chemicals being phased out.

7.5 Plant Location and Distribution

Because of the risk involved with producing a single product, it is assumed that the companies that purchase this technology will create an extension to their already established plant when making Flame-O 1000™. Since KSMH is targeting computer manufacturers, the plant location of these manufacturers needed to be determined. KSMH discovered that the main source of computer employment was in the state of Texas, which is shown in Figure 16.

U.S. Computer Employment Vs. Texas Computer Employment

Index, January 1993 = 100



NOTE: U.S. series taken from SIC 3571, Electronic Computer Manufacturing; Texas series taken from NAICS 3341, Computer and Peripheral Equipment Manufacturing.

SOURCE: Bureau of Labor Statistics.

Figure 16: US Computer Employment vs. Texas Computer Employment²⁷

Hewlett-Packard/Compaq is based in Houston, Texas and is responsible for 44% of Texas computer employment. Dell Computers is also based in Texas in Austin; however, they are responsible for 52% of Texas computer employment.

Distribution of the flame-retardant will be left to the decision of the manufacturer. KSMH suggests that Flame-O 1000TM be stored within the facility so the customer's demands can be met as soon as possible. It should be shipped directly from the warehouse to ensure the safe handling of Flame-O 1000TM.

7.6 Target Company

The company the KSMH is trying to acquire as a valued client is Dell Computers. Dell Computers is a major contributor in the electronic/computer industry. They sell a variety of electronic devices with plastic housings that Flame-O 1000™ can be incorporated into such as desktop computers, laptop computers, printers, and MP3 players. Also, Dell Computers has a convenient plant location.

8.0 Operations / Production

8.1 Suppliers

The client's manufacturing company will be working on a continuous basis with the raw materials' distributor and hope to develop a business discount for bulk purchases since they will be the sole supplier. Inventories of the raw materials should be made bi-weekly to ensure the success of the Flame-O 1000TM production.

8.2 Plant Design

The proposed plant design involves a CSTR, two flash drums and three storage tanks. The first tank is for the storage of the disposal HCl, the second for the recycle and the third for the product. The design is shown below in Figure 17.

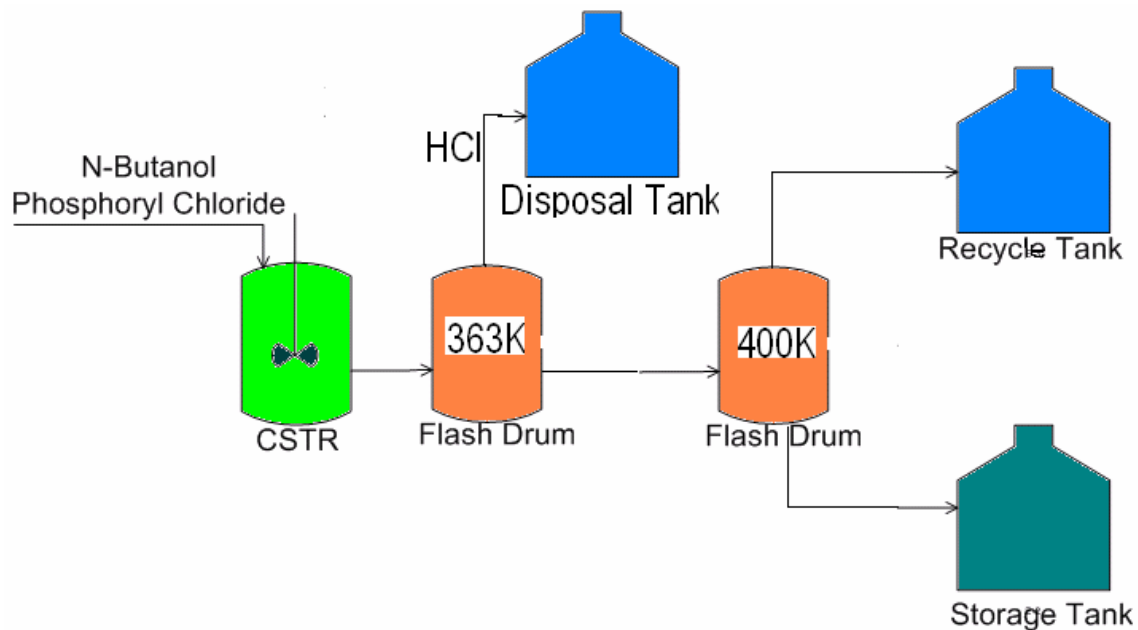


Figure 17: Plant Design

The raw materials, n-butanol and phosphoryl chloride, enter the Continuous Stir Tank Reactor (CSTR) with an inlet temperature and pressure of 25°C and 14.7psia,

respectively. The efficiency of the reaction is assumed to be about 80%. Thus, the components at the outlet of the CSTR are tri-n-butyl phosphate, hydrogen chloride, n-butanol and phosphoryl chloride. The boiling points of these components, shown in Table 17 below, were used for flash calculations.

Table 17: Boiling Points

| Chemicals | Boiling Point |
|-----------------------|----------------------|
| HCl | 84.5°C |
| POCl ₃ | 105°C |
| n - Butanol | 118°C |
| Tri-n-butyl Phosphate | 289°C |

These components are fed into a flash drum and heated to 90°C. Because the HCl has the lowest boiling point, HCl will vaporize and go to the Disposal Tank. The other products will go to the next flash drum, which is heated at 127°C, so that n-butanol and phosphoryl chloride are boiled and transferred to Recycle Tank. TBP will stay in liquid phase and go to the Storage Tank.

8.3 Production Capacity

There were 7 different capacities calculated. The cost of equipments and raw materials for different flow rates used in plan design is shown in the Tables 18 and 19:

Table 18: Cost of Raw Materials

| | Product kg/yr | n-Butanol kg/yr | POCl3 kg/yr | Total cost |
|---|----------------------|------------------------|--------------------|-------------------|
| 1 | 1,110,000 | 1,160,000 | 800,000 | \$ 2,785,302 |
| 2 | 1,230,000 | 1,280,000 | 886,000 | \$ 3,086,416 |
| 3 | 1,540,000 | 1,610,000 | 1,110,000 | \$ 3,864,293 |
| 4 | 1,700,000 | 1,770,000 | 1,220,000 | \$ 4,265,779 |
| 5 | 1,850,000 | 1,930,000 | 1,330,000 | \$ 4,642,171 |
| 6 | 2,090,000 | 2,180,000 | 1,510,000 | \$ 5,244,398 |
| 7 | 2,500,000 | 2,610,000 | 1,800,000 | \$ 6,273,204 |

Table 19: Cost of Equipment

| | V_{Batch Reactor} m³ | \$ | 2 V_{flash Drum} m³ | \$ | 3 Storage tank (500m3) | Total equipment cost |
|---|--|-----------|---|-----------|-----------------------------------|---------------------------------|
| 1 | 3.13 | \$38,802 | 3.13 | \$47,000 | \$ 355,986 | \$ 441,788 |
| 2 | 3.79 | \$42,936 | 3.79 | \$48,000 | \$ 375,555 | \$ 466,491 |
| 3 | 5.71 | \$53,333 | 5.71 | \$50,600 | \$ 395,124 | \$ 499,057 |
| 4 | 7.00 | \$59,403 | 7.00 | \$51,800 | \$ 414,693 | \$ 525,896 |
| 5 | 8.22 | \$64,673 | 8.22 | \$52,800 | \$ 434,262 | \$ 551,735 |
| 6 | 10.34 | \$73,021 | 10.34 | \$74,200 | \$ 453,831 | \$ 601,052 |
| 7 | 14.10 | \$86,043 | 14.10 | \$80,200 | \$ 473,400 | \$ 639,643 |

When the capacity increases from 1,110,000 to 2,500,000 kg/year, the cost of equipment and raw materials also increases. These trends are shown below in Figures 18 and 19.

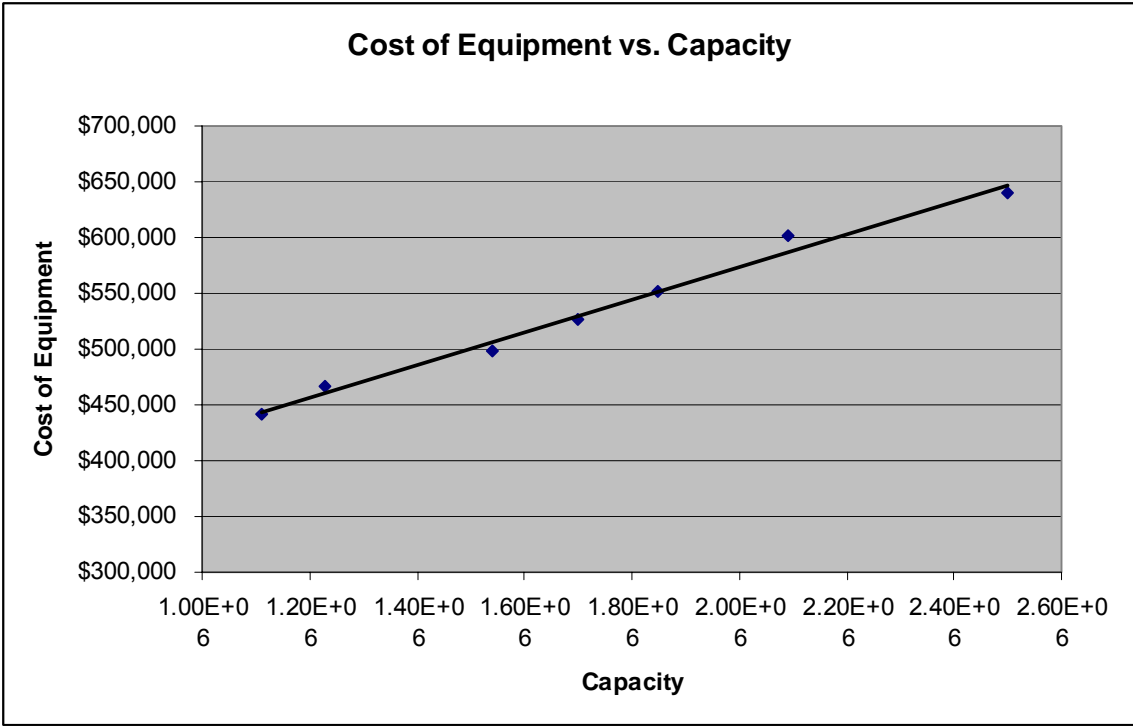


Figure 18: Cost of Equipment vs. Capacity

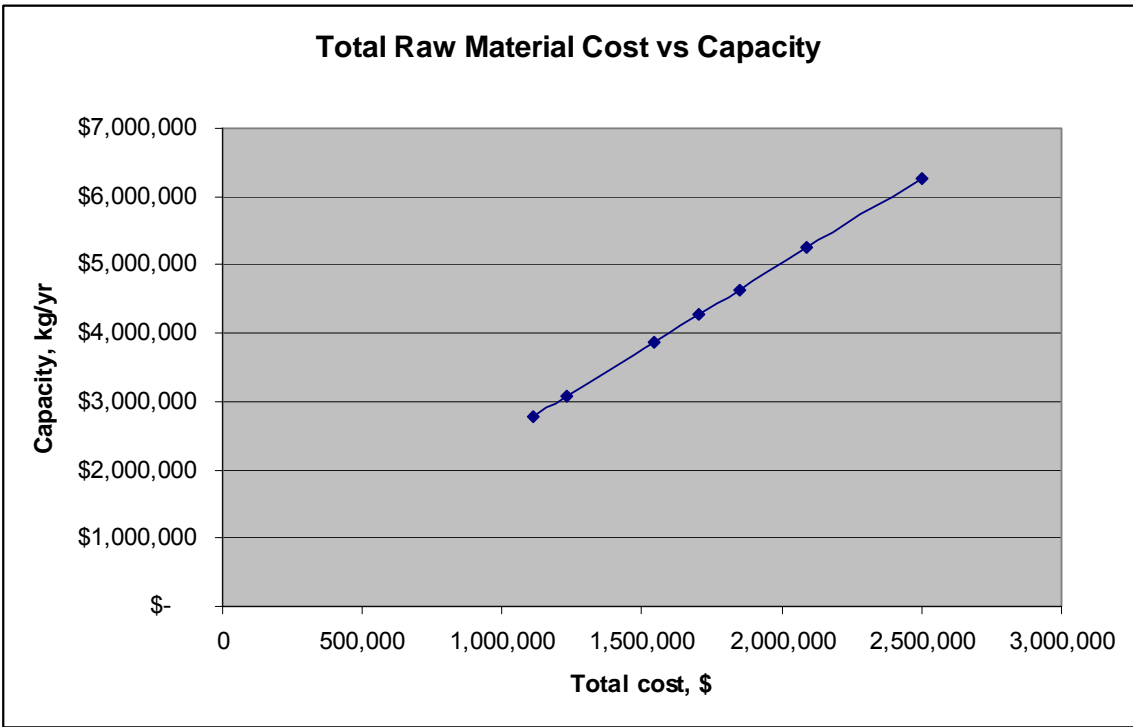


Figure 19: Total Raw Material Cost vs. Capacity

9.0 Investment Opportunity

9.1 Initial Investment

KSMH proposes that an investment of \$4,000,000 be provided to license the chemical modeling of Flame-O 1000TM. Once the payment is received in full, KSMH will begin construction on the addition to their plant. Construction is expected to take no longer than 6 months. KSMH requires that our company will be entitled to a stipend of 10% of the revenue after the completion of the first fiscal year, then a salary of 5% of the revenue for each additional year for the first 10 years. This salary will guarantee Flame-O 1000TM consultation from KSMH's engineers. KSMH requires the signing of a non-disclosure agreement stating that the contents of this business plan will not be reproduced or disclosed to anyone without KSMH's expressed, written permission.

9.2 Net Present Worth

The production cost estimation of Flame-O 1000TM was designed as an addition to an existing facility. KSM decided to assume a capacity of 1,850,000 kg/yr of Flame-O 1000TM to meet the demands of the flame-retardant market after the phasing out of the penta- and octa- bromodiphenyl ethers. A more detailed reasoning for this capacity was explained in Section 9.3 Risk and Uncertainty. The cost of electricity is based on the duty of the CSTR and flash drums. The operating labor is 3 to 6 workers per shift and 3 shifts per day. KSMH recommends five non-salary workers at \$15/hr and one salary worker at a salary of \$80,000/yr. The cost analysis was projected over a 10 year period. The Fixed Capital Investment included the licensing fee of \$4 million.

The Total Capital Investment was calculated to be \$5.5 million, which includes the purchase of equipment, installation, and construction. The company is expected to run 95% of the year, which is 347 days. KSMH assumed straight line depreciation over a ten-year period and that the income tax is 35% of the revenue. A detailed cost analysis is provided below in Table 20.

Table 20: Cost Analysis

| | FCI | TCI | Return on Investment %/y | NPW |
|---|--------------|--------------|---------------------------------|---------------|
| 1 | \$ 5,003,264 | \$ 5,180,428 | 17.99 | \$ 1,669,770 |
| 2 | \$ 5,065,119 | \$ 5,253,205 | 31.44 | \$ 5,245,383 |
| 3 | \$ 5,166,131 | \$ 5,372,054 | 60.48 | \$ 13,062,043 |
| 4 | \$ 5,239,272 | \$ 5,458,112 | 76.68 | \$ 17,616,713 |
| 5 | \$ 5,307,425 | \$ 5,538,300 | 87.23 | \$ 20,746,777 |
| 6 | \$ 5,449,191 | \$ 5,705,099 | 109.20 | \$ 27,527,987 |
| 7 | \$ 5,574,180 | \$ 5,852,160 | 143.73 | \$ 38,179,620 |

The average return on investment for all capacities was calculated to be 75% over a ten-year period. The ROI is high, because of the low cost of equipment. The primary expense is the cost of raw materials. The cost of raw materials is \$3.7 million for the production of 1,850,000 kg/year of Flame-O 1000TM. The Net Present Worth after ten years was calculated to be \$20.7 million.

9.3 Risk and Uncertainty

When creating a new product, it is important to take into consideration the risk involved with the venture. For the risk analysis in this process, a base product production capacity was created. The capacity was picked by taking the available United States market, 1.1 billion pounds of product, and multiplying by 39%, the

weight percent brominated flame-retardants. This value was then multiplied by 20%, the assumed fraction that will be missing due to the ban/phase out of penta- and decabrominateddiphenyl ether, and then 3.5%, the fraction of the market our product will hopefully replace. Based on this result, KSMH proposed a base capacity of 1,230,000 kg/year with a standard deviation of 30% for both the capacity and product price. The net present worth for all 7 capacities was exported to create risk curves. The product-selling price was assumed to be \$10/kg based on values provided for phosphorus flame-retardants sold by Great Lakes Chemical, Flame-O 1000TM's largest competitor²⁴. Seven risk curves were produced, using a range of 1,110,000 to 2,500,000 kg/year. The graph of risk curves is provided below in Figure 20.

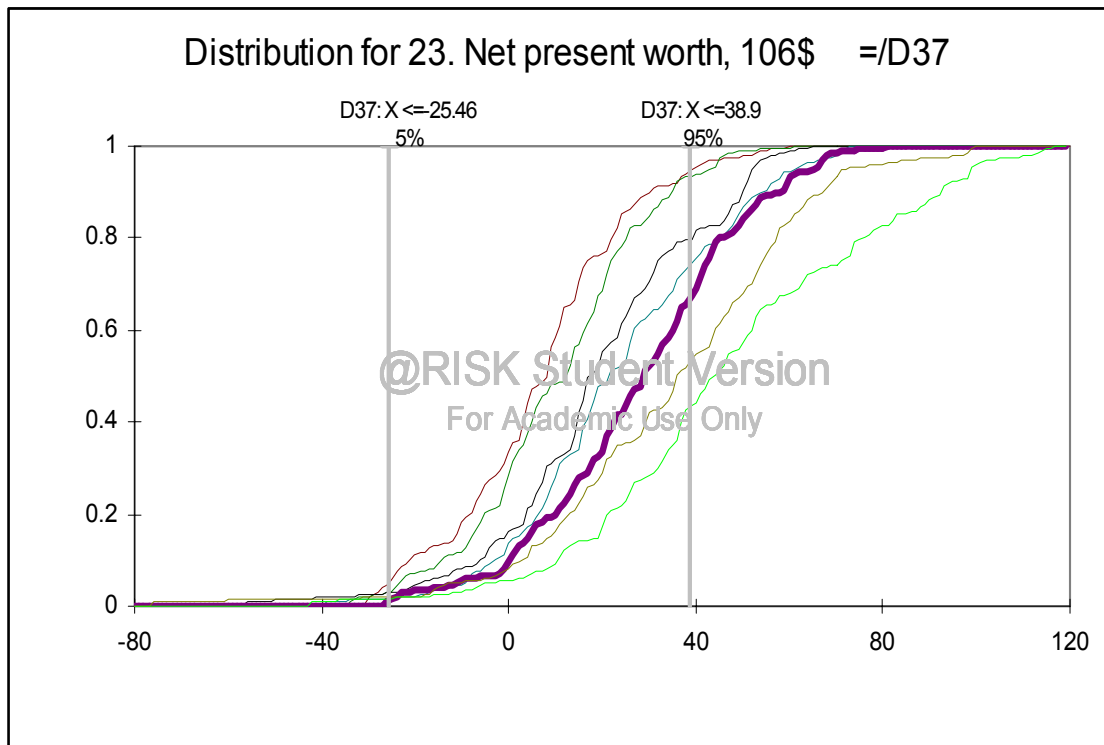


Figure 20: Risk Curves

The capacities #6 and #7 are discarded since they have unreasonably high ROI. Therefore, the capacity #5 (1.85 million kg/yr) was chosen as the most profitable venture with the least amount of risk.

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11.0 Appendix A

Molecular Discovery

Group Contribution Equations Used:

$$T_c = \left[\frac{T_b}{0.567 + \Sigma\Delta_T - (\Sigma\Delta_T)^2} \right] \quad \text{Eq. 2-3} \quad \text{Lydersen Method}$$

$$P_c = \frac{0.101325 \cdot M}{(0.34 + \Sigma\Delta_p)} \quad \text{Eq. 2-7} \quad \text{Lydersen Method}$$

$$V_c = 0.040 + \Sigma\Delta_v \quad \text{Eq. 2-14} \quad \text{Lydersen Method}$$

$$\log P_r^{\text{sat}} = -\phi(T_r) - (\alpha - 7) \cdot \psi \cdot (T_r) \quad \text{Eq. 2-39} \quad \text{Riedel Method}$$

$$\zeta(T_r) = \frac{36}{T_r} + 96.7 \cdot \log_{10} T_r - 35 - T_r^6$$

$$\phi(T_r) = 0.118 \cdot \zeta(T_r) - 7 \cdot \log_{10} T_r$$

Eq. 2-40:2-43 Riedel Method

$$\psi(T_r) = 0.0364 \cdot \zeta(T_r) - \log_{10} T_r$$

$$\alpha = \frac{0.136 \cdot \zeta(T_{r_b}) + \log_{10} P_c - 5.01}{\psi(T_{r_b})}$$

Variable Definitions:

T_c – Critical Temperature

T_b – Normal Boiling Temperature

$\Sigma\Delta_T, \Sigma\Delta_p, \Sigma\Delta_v$ – Sums of Lydersen group contributions

M – Molecular Weight

P_r – Reduced Pressure = P/P_c

P^{sat} – Saturated vapor pressure at a given temperature

T_r – Reduced Temperature = T/T_c

T_{r_b} – Reduced Normal boiling temperature = T_{boil}/T_c

Group Contribution Equations Used (Boethling and Mackay):

$$T_b = 198.2 + \sum n_i (\Delta T_b)_i \quad \text{Eq. 2.7} \quad \text{Stein and Brown}$$

$$T_b(\text{corr}) = T_b - 94.84 + 0.5577 \cdot T_b - 0.0007705 \cdot T_b^2$$

For $T_b \leq 700\text{K}$ Eq. 2.8 Stein and Brown

$$T_b(\text{corr}) = T_b + 282.7 - 0.5209 \cdot T_b$$

For $T_b \geq 700\text{K}$ Eq. 2.9 Stein and Brown

$$T_m = 122.5 + \sum (n_i \cdot g_i) \quad \text{Eq. 1.27} \quad \text{Jobak and Reid}$$

Variable Definitions:

- T_b – “Raw” boiling point
- n_i – Number of times group i appears in molecule
- $(\Delta T_b)_i$ – Group contribution to molecular boiling point
- $T_b(\text{corr})$ – “Temperature Corrected” boiling point
- T_m – Melting point
- g_i – Group contribution to molecular boiling point

Table A1: Predicted Properties of Simulated Molecules

| Rank | CAS # | Molecule | T_c eq 2-3 | P_c (MPa) eq 2-7 | V_c (m ³ /kmol) Eq 2-14 | (± 10 - 30%) | Diffusivity in water eq 2-159 |
|------|----------|------------------------------------|-----------------|--------------------------|--|--------------------------|-------------------------------------|
| | | | | | | Vap P @ 513K (MPa) | |
| 1 | 126-73-8 | Tri-n-Butyl Phosphate | 800.5 | 1.379 | 0.959 | 0.0019 | 7.029E-07 |
| 3 | 513-02-0 | **Tri-Isopropyl Ester | 771.1 | 1.667 | 0.782 | 0.2556 | 7.941E-07 |
| 2 | 78-40-0 | Tri-ethyl Phosphate | 804.8 | 1.969 | 0.629 | 0.1996 | 9.050E-07 |
| ** | 126-72-7 | Tris(2,3ibromopropyl) phosphate | 613.1 | 1.579 | 0.782 | 6.05 x10 ⁶ | 7.941E-07 |

Economic Equations Used

$$NPW = \sum \frac{CF_k}{(1+i)^k} + \frac{CF_n + V_s + I_w}{(1+i)^n} - TCI$$

Where NPW is the Net Present Worth, TCI is the total capital investment, V_s is the salvage value, I_w is the working capital and CF is the cash flow for the independent years. Basic relationships for TCI and Total Product cost based on equipment cost were found in *Plant Design and Economics for Chemical Engineers* by Peters, Timmerhaus and West.

12.0 Appendix B

12.1 Testing of Synthesis Reaction

12.1.1 Safety

Safety Goggles
Face Shield
Protective Clothing
Fume Hood/Ventilation System

12.1.2 Materials

N-Butanol (10 mL/experiment)
Phosphoryl Chloride (35 mL/experiment)
Standard Laboratory Glassware
-Beaker (50 mL)
Hot plate with stirrer
Thermometer

12.1.3 Background

This reaction occurs at room temperature or slightly above. The best temperature at which the reaction should occur is unknown, so the boiling temperatures of the three chemicals are provided below. All three are liquids at room temperature.

| Chemical | Molecular Weight | Specific Gravity | Boiling Temperature | Polarity |
|-----------------------|------------------|------------------|---------------------|-----------------|
| N-Butanol | 74.12 | 0.81 | 242 °F | Most Polar |
| Phosphoryl Chloride | 153.33 | 1.645 | 222 °F | Least Polar |
| Tri-n-butyl Phosphate | 266.32 | 0.977 | 331°F | Middle Polarity |

Basic Kinetics data is provided below:

Zero-order reactions ($-r_A = k$):
CA vs Time

First-order reactions ($-r_A = kC_A$):
 $\ln\left(\frac{CA_0}{CA}\right)$ vs. Time

Second Order Reactions ($-r_A = kC_A^2$):

$\frac{1}{CA}$ vs. Time

Using this rate, the activation order can be found by using the rate law and knowing that $r = A \exp(-E_a/RT)$

where A is a constant, E_a is the activation energy, R is the universal gas constant and T is the temperature.

Noting that both reactants boil around 220 °F, the reaction must occur below 200 °F.

To determine both the temperature at which it should be heated, and the time needed to create the product, the following procedure should be followed:

12.1.4 Procedure

Test at room temperature (70°F)

1. Place 35 mL of n-butanol in a 50 mL beaker
2. Quickly bring to the desired temperature and hold constant (step only used for tests above room temperature)
3. Add 10mL phosphoryl chloride and begin stirrer
4. Heat for 1 hour, taking samples for gas/liquid chromatography every 30 seconds including the original concentration
5. Repeat above procedure at 75 °F, 80 °F, etc until 200 °F

From gas/liquid chromatography the concentration will be determined. Several plots will then be formed to determine the reaction order; the one that is linear proves to be the correct order for the reaction, all at the different temperatures.

12.2 Testing as a Coating

12.2.1 Safety

- Safety Goggles
- Face Shield
- Protective Clothing
- Fume Hood/Ventilation System

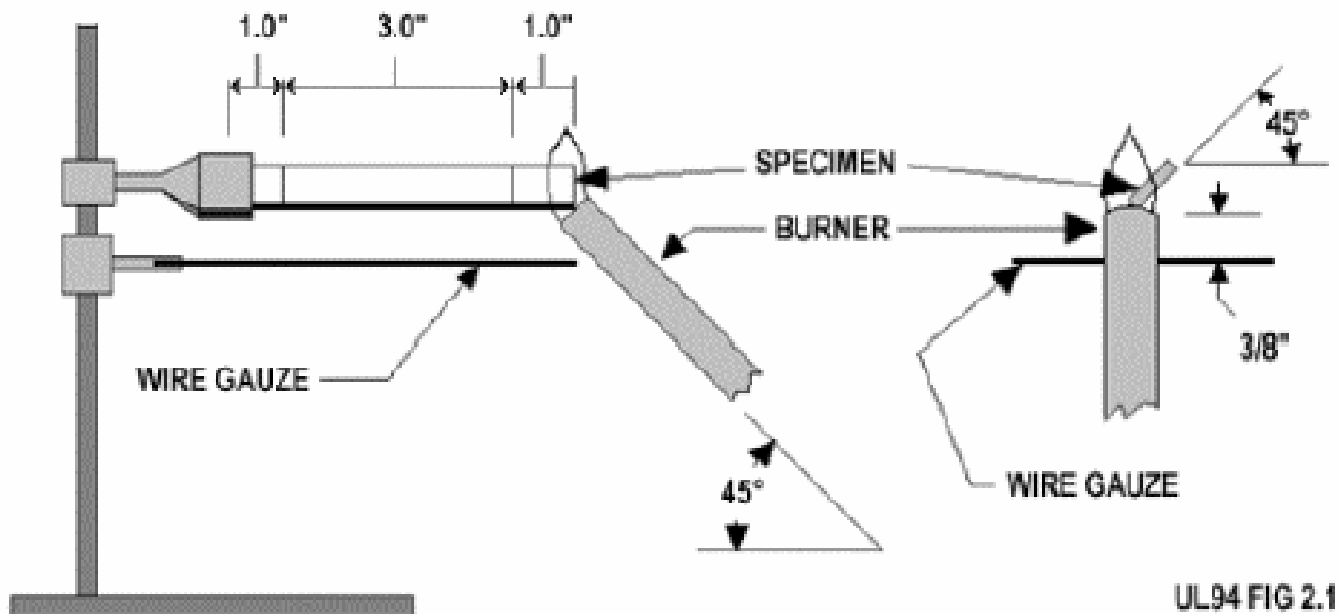
12.2.2 Materials

- Thermometer
- 5 pieces of plastic, 10g in weight, melted into a rectangle
- Tri-n-butyl phosphate (10ml/experiment run)
- Acetylene Torch
- Metal Screen
- Stand for Metal Screen

12.2.3 Procedure

- Leave one sample normal (Sample 1)
- Coat samples 2-5 with tri-n-butyl phosphate
 - Sample 2 with .5ml
 - Sample 3 with 1ml
 - Sample 4 with 2ml
 - Sample 5 with 4ml

Set up the stand with the screen horizontal to the table
Set up the Acetylene Torch so that the flame comes in from the side but still heats the samples from beneath. See figure below (*Flammability Testing*²⁶):



UL94 FIG 2.1
HORIZONTAL BURNING TEST FOR 94HB CLASSIFICATION

Place all five samples on the metal screen
Bring the temperature up slowly and watch for changes in each sample
-noting the temperatures at which they melt/burst into flames and how they relate to Sample 1

Take pictures in 10-second increments of all 5 samples

Repeat 4 more times to confirm data

12.3 Testing as an Additive

12.3.1 Safety

Safety Goggles
Face Shield
Protective Clothing
Fume Hood/Ventilation System

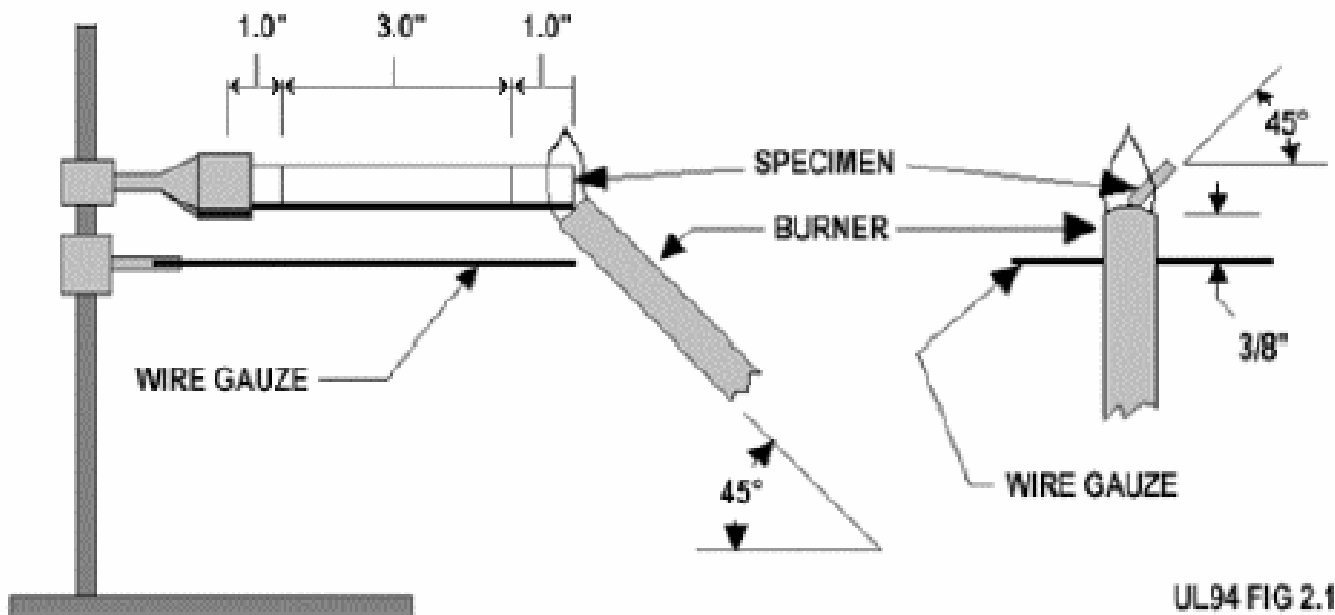
12.3.2 Materials

Thermometer
5 -10g in weight to be melted into rectangles
Tri-n-butyl phosphate (10ml/experiment run)
Acetylene Torch
Metal Screen
Stand for Metal Screen

12.3.3 Procedure

Melt the 10g
Leave one sample normal (Sample 1)
Melt in tri-n-butyl phosphate into samples 2-5
-Sample 2 with 5-wt% TBP (0.5mL)
-Sample 3 with 10-wt% TBP (1mL)
-Sample 4 with 15-wt% TBP (1.5mL)
-Sample 5 with 20-wt% TBP (2mL)

Set up the stand with the screen horizontal to the table
Set up the Acetylene Torch so that the flame comes in from the side but still heats the samples from beneath. See figure below:



UL94 FIG 2.1
HORIZONTAL BURNING TEST FOR 94HB CLASSIFICATION

Take pictures in 10-second increments of all 5 samples
Place all five samples on the metal screen

Bring the temperature up slowly and watch for changes in each sample
-noting the temperatures at which they melt/burst into flames and how they relate to Sample 1

Repeat 4 more times to confirm data

Appendix B 12.4.0 Qualitative Testing

12.4.1 Safety

- Safety Goggles
- Face Shield
- Protective Clothing
- Fume Hood/Ventilation System

12.4.2 Materials

- 3 pieces of plastic, 10g in weight, melted into a rectangle
- Tri-n-butyl phosphate (5ml/experiment run)
- Acetylene Torch
- Metal Screen
- 2 Bricks for Metal Screen to be placed on
- Aluminum foil

12.4.3 Procedure

Leave two samples normal (Samples 1 and 2)

Coat sample 2 with tri-n-butyl phosphate
Melt in tri-n-butyl phosphate for samples 3

Set up the two bricks supporting the screen horizontal to the table
Set up the Acetylene Torch so that the flame comes in from the side but still heats the samples from beneath. See Figure B1 below:

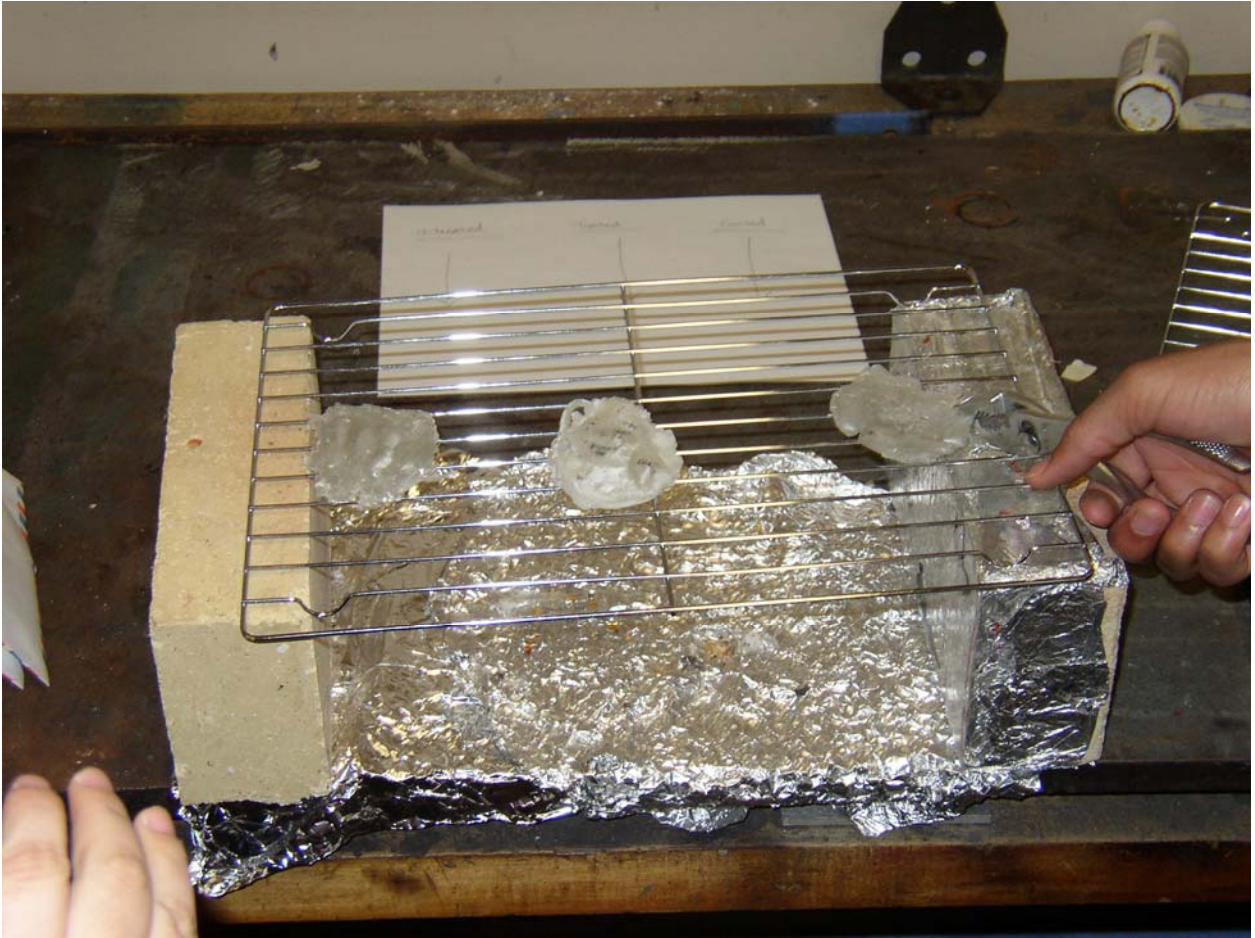


Figure B1: Experiment Set-up

Place all 3 samples on the metal screen, with the regular sample on the far left, the mixed, or treated, sample in the middle, and the coated sample on the far right. See Figure B1 above.

Beneath each sample, place the acetylene torch and wave it back and forth in a constant motion. Continue to do this until the sample bursts into flames, see Figure B2 below. Record times until it melts completely and when the flame goes out.



Figure B2: Flame Testing

Repeat 3 more times to confirm data.

Appendix B 12.5 (from *Flammability Testing*²⁶)

B12.5.1 ASTM Tests

B12.5.1.1 Flammability Test (ASTM D 568 for flexible plastics and D 635 for self-supporting plastics)

ASTM D 568 supports the sample vertically, whereas D 635 supports the sample horizontally. A flame from a Bunsen burner is exposed to a plastic test bar for seconds. The sample is allowed to burn until it either extinguishes itself or burns past a gage mark (100 mm) on the bar. If the sample does not burn past the 100 mm gage mark, time extent of burning are reported. If it burns past the gage mark, and average burn rate, in centimeters per minute, is reported. Materials that do not burn to the gage mark are said to be self-extinguishing.

B12.5.1.2 Oxygen Index Test (ASTM D 2863)

This tests the minimum concentration of oxygen in a pure oxygen/nitrogen environment that is necessary for the sample to maintain combustion. The sample is hung vertically in a special chamber, and then ignited. The oxygen concentration is then reduced until the combustion is just maintained. The Limiting Oxygen Index (LOI) represents this percentage of oxygen.

B12.5.1.3 Radiant Panel Test (ASTM E 162)

A radiant panel is maintained at 670C (1238F) as a heat source to ignite a plastic sheet. The plastic sheet (152mm x 457mm, 6" x 18") is maintained at a set distance from the panel, with the top tilted at a 30 angle toward the panel. The rate of burning

and the heat evolved in the burning are measured and combined to form a flame-spread index.

B12.5.1.4 Smoke Density Test (ASTM D 2843)

This test measures the loss of light transmission through smoke produced from a burning plastic. A sample is burned inside of a special chamber. A light is passed between two photoelectric cell plates, and the transmission is plotted against time. The area under this curve is the total smoke produced.

B12.5.2 Underwriters Laboratory Tests

B12.5.2.1 UL 94 Flammability Tests

The Underwriters Laboratories have developed a series of flammability tests, all designated under UL 94. For a plastic to receive a certain UL rating, it must pass certain criteria of a test. The different ratings are outlined below.

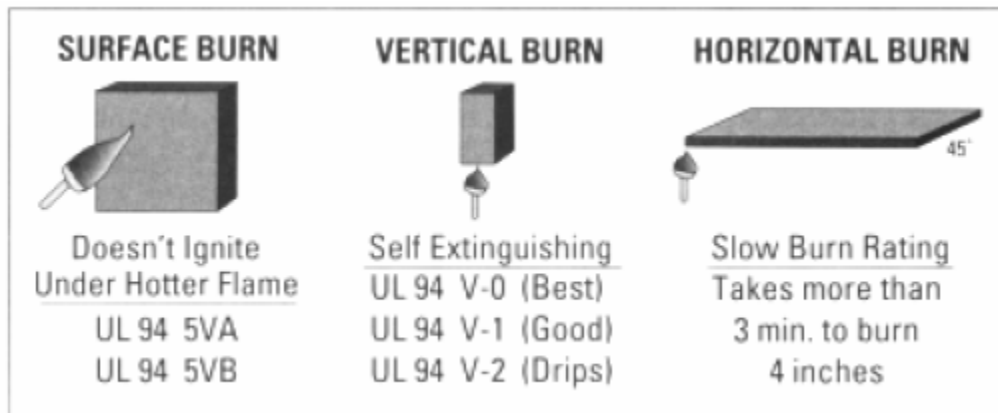


Table B1: UL 94 Flammability Ratings Description

| | |
|---------------------|---|
| 5VA Surface Burn | Burning stops within 60 seconds after five applications of five seconds each of a flame (larger than that used in Vertical Burn testing) to a test bar. Test specimens MAY NOT have a burn-through (no hole). This is the highest (most flame retardant) UL94 rating. |
| 5V B Surface Burn | Burning stops within 60 seconds after five applications of five seconds each of a flame (larger than that used in Vertical Burn testing) to a test bar. Test specimens MAY HAVE a burn-through (no hole). |
| V-0 Vertical Burn | Burning stops within 10 seconds after two applications of ten seconds each of a flame to a test bar. No flaming drips are allowed. |
| V-1 Vertical Burn | Burning stops within 60 seconds after two applications of ten seconds each of a flame to a test bar. No flaming drips are allowed. |
| V-2 Vertical Burn | Burning stops within 60 seconds after two applications of ten seconds each of a flame to a test bar. Flaming drips ARE allowed. |
| H-B Horizontal Burn | Slow horizontal burning on a 3mm thick specimen with a burning rate is less than 3"/min or stops burning before the 5" mark. H-B rated materials are considered "self-extinguishing". This is the lowest (least flame retardant) UL94 rating. |

B12.5.2.2 94 HB Horizontal Burn Test

This is the easiest flammability test for a material to pass. Generally, a 94HB requirement will be recognized if the materials passed any of the V tests. The 94HB rating is generally suitable for attended, portable, intermittent-duty, household appliance enclosures, like hair dryers.

Refer to Figure B3 for the experimental setup. A ½" x 5" sample is clamped on a ring stand. Marks are made on the sample 1" and 5" from the free end. A flame is applied to the sample for 30 seconds or until the sample burns past the 1" mark. The sample is allowed to burn until it stops or reaches the 5" mark. If the sample burns up

to the 5" mark, a burn rate is calculated. If the sample stops burning before the 5" mark, the burn time and the length of the damaged section between the marks is reported.

A material that is less than 0.118" receives a 94HB classification if it burns at a rate of less than 3" per minute or stops burning before the 5" mark. Three samples are tested. If only one of them fails, another set of three is tested, and all must pass for the part to receive 94HB certification.

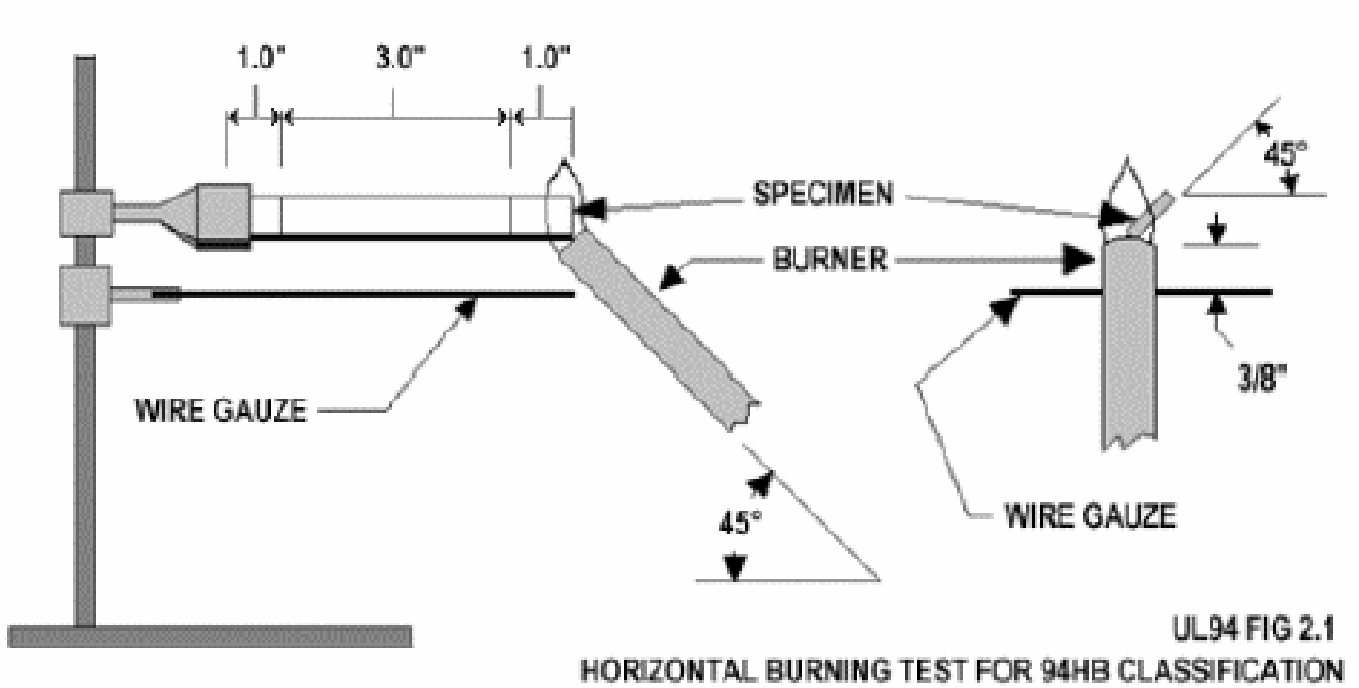


Figure B3: Setup for UL 94HB testing

B12.5.2.3 94V Vertical Burning Test

This test can yield three designations: 94V-0, 94V-1 and 94V-2. These ratings would be suitable for an unattended, portable, intermittent-duty, and household appliance enclosure, like a coffee maker.

See the left side of Figure B4 for the experimental setup. A ½” x 5” sample is held in the vertical position with cotton placed directly under the specimen. A burner flame is then applied to free end for 10 seconds two times. The second burn is done when the flaming combustion from the first 10 second burn stops. The sets of five specimens are tested. The following values are recorded.

- Duration of flaming combustion after the first burner flame application.
- Duration of flaming combustion after second burner flame application.
- Duration of glowing combustion after second burner flame application.
- Whether or not flaming drips ignite cotton placed below specimen.
- Whether or not specimen burns up to holding clamp.

| Criteria Conditions for 94V Ratings | 94V-0 | 94V-1 | 94V-2 |
|--|--------------|--------------|--------------|
| Total flaming combustion for each specimen | 10s | 30s | 30s |
| Total flaming combustion for all 5 specimens of any set | 50s | 250s | 250s |
| Flaming and glowing combustion for each specimen after second burner flame application | 30s | 60s | 60s |
| Cotton ignited by flame drips from any specimen | No | No | Yes |
| Glowing or flaming combustion of any specimen to holding clamp | No | No | No |

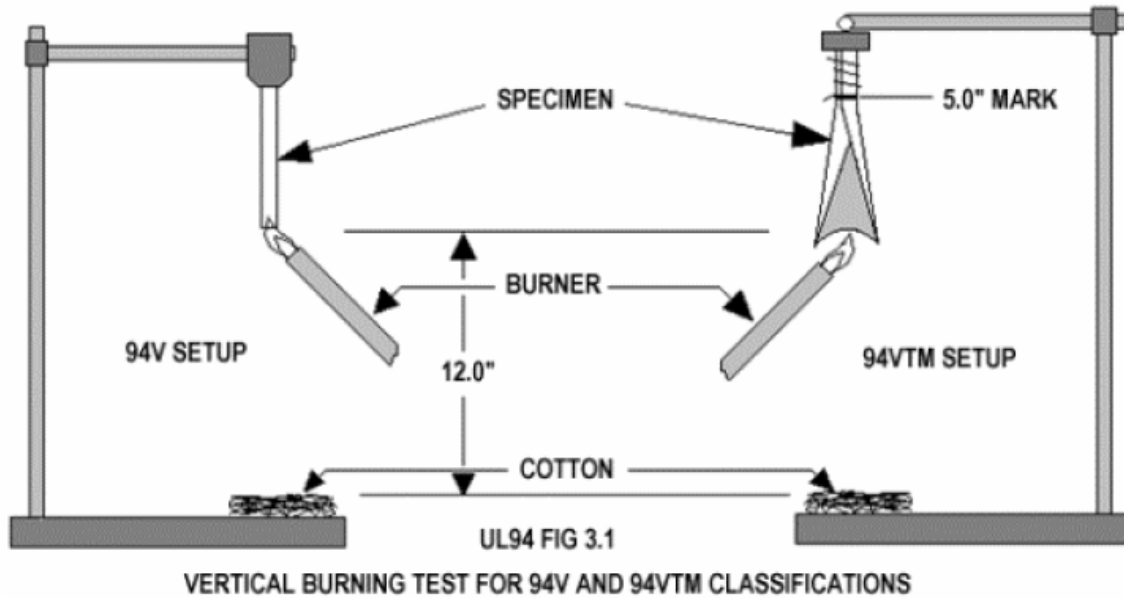


Figure B4: Setup for UL 94V testing

B12.5.2.4 94VTM Vertical Thin Material Test

A material can be too thin for the standard 94V test because it may distort, shrink, or flex during the burn test. There is another similar test for these thin materials, which are generally less than 0.010" thick.

Refer to the right side of Figure B4. An 8" x 2" sample is wrapped around a 1/2" mandrel, and then taped on one end. The mandrel is removed; leaving a cone-shaped sample that is relatively rigid. The two flame applications are 3 seconds instead of 10 seconds. All of the other criteria from the 94V test apply, except that no specimens can have flaming or glowing combustion up to a mark 5" from the bottom of the sample.

Table A2: Sample Calculation of Lydersen Group Contributions

Lydersen Method --

| Group Number | Group Description | Δ_T | Δ_P | Δ_V | M | Quant. | C_s | Δ_s | sum N_f | sum N_s | sum N_g | $\Sigma\Delta_T$ | $\Sigma\Delta_P$ | $\Sigma\Delta_V$ | ΣM | |
|--------------|-------------------|------------|------------|------------|--------|--------|-------|------------|-------------|----------------|----------------|------------------|------------------|------------------|--------------|----------------|
| 1 | --CH3 | 0.020 | 0.227 | 0.055 | 15.034 | 0 | 1 | 18.33 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | |
| 2 | >CH2 | 0.020 | 0.227 | 0.055 | 14.026 | 6 | 1 | 9.41 | 56.46 | 56.46 | 56.46 | 0.12 | 1.362 | 0.33 | 84.156 | |
| 3 | >CH-- | 0.012 | 0.21 | 0.051 | 13.018 | 3 | 0.69 | -16.19 | -48.57 | 33.5133 | -48.57 | 0.036 | 0.63 | 0.153 | 39.054 | |
| 4 | >C< | 0.000 | 0.21 | 0.041 | 12.01 | 0 | 0.67 | -38.7 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | |
| 5 | =CH2 | 0.018 | 0.198 | 0.045 | 14.026 | 0 | 1 | 14.56 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | |
| 6 | =CH-- | 0.018 | 0.198 | 0.045 | 13.018 | 0 | 3.23 | 4.85 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | |
| 7 | =C< | 0.000 | 0.198 | 0.036 | 12.01 | 0 | 1 | -11.38 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | |
| 8 | =C= | 0.000 | 0.198 | 0.036 | 12.01 | 0 | 0 | | 0 | 0 | 0 | 0 | 0 | 0 | 0 | |
| 9 | (triple bond)CH | 0.005 | 0.153 | 0.036 | 13.018 | 0 | 1 | 10.88 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | |
| 10 | (triple bond)C-- | 0.005 | 0.153 | 0.036 | 12.01 | 0 | 1 | 2.18 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | |
| 10.5 | O=P≡ | -0.142 | 0.879439 | 0.259401 | 46.973 | 1 | 0 | 41.7535 | 41.7535 | 0 | 0 | 0.142 | 0.879 | 0.259 | 46.973 | |
| | | | | | | | | | SUMS | 33.8635 | 22.9467 | 7.89 | 0.014 | 2.87 | 0.742 | 170.183 |