Flame Retardants

Group 4—April 8th

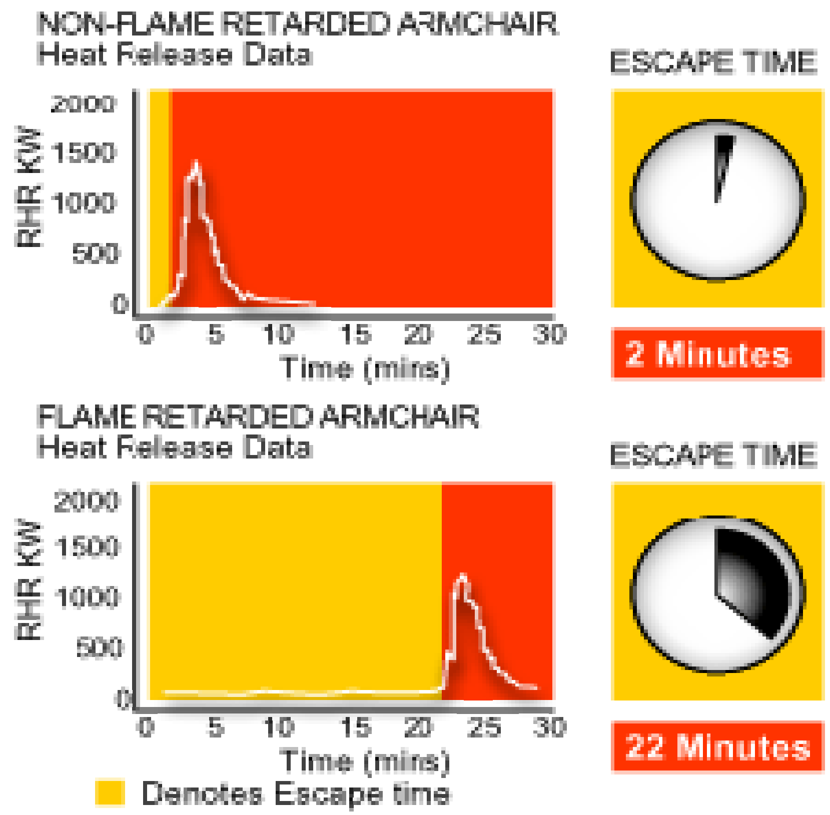
Danielle Keese
Jeff Mueggenborg
Esan Savannah
Ha Nguyen

Dangers of Fire (United States in 2002)

- Someone died in a fire every 3 hrs and someone was injured every 37 minutes
- 401,000 home fires
- Residential fires caused more than $6.1 billion in property damage

What is a Flame Retardant?

- A chemical added to combustible materials to render them more resistant to ignition
- Minimizes the risk of fire starting
- Increases the safety of lives and property



What is a Flame Retardant?

- 4 major family of Flame Retardant
- Provides for a safer material without compromising performance
- Flame retardants work to slow or stop the combustion cycle

Combustion Cycle

- Flammable materials are decomposed to release energy in the form of heat and light
- Combustion of hydrocarbon:

$$C_xH_y + O_2 \xrightarrow{spark} nCO_2 + n'H_2O + \Delta H$$

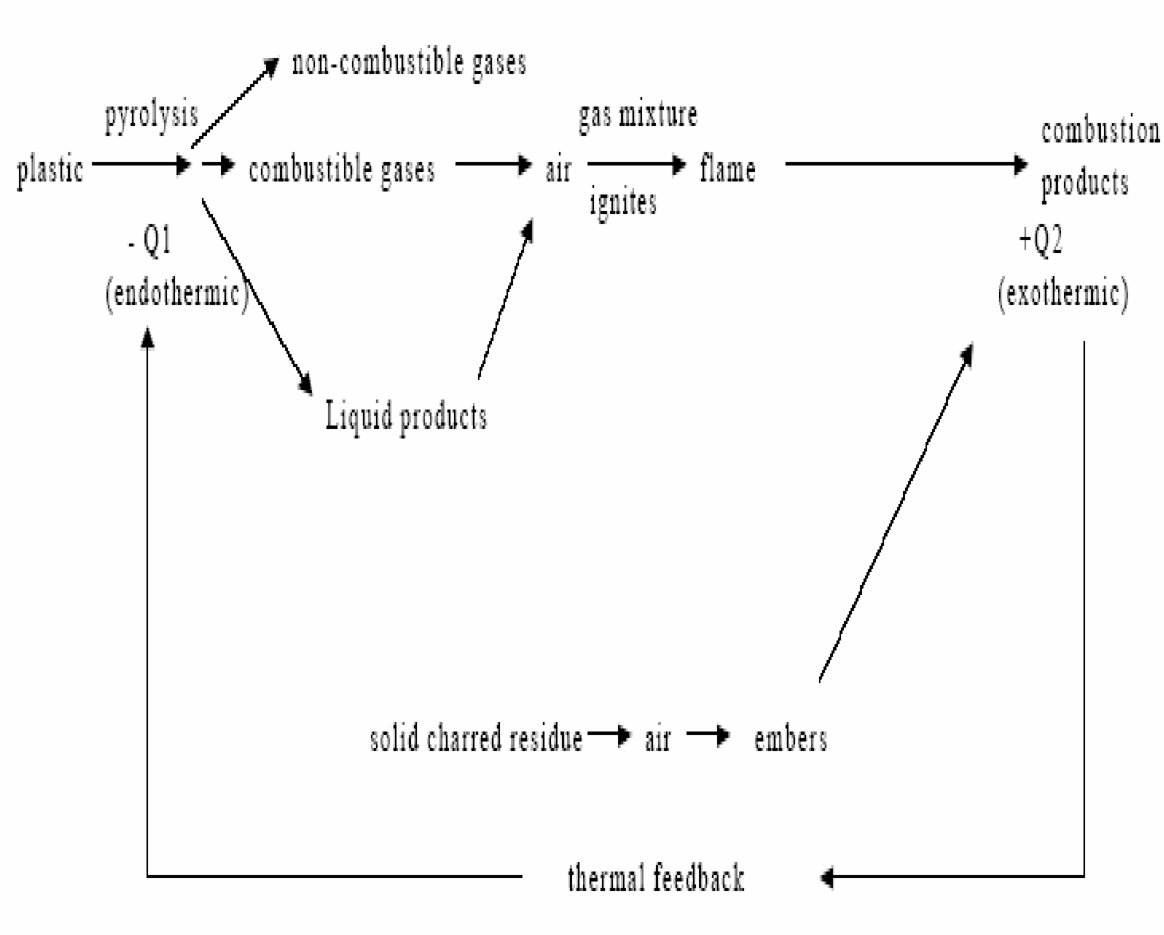
- Examples of combustion:
  - Phosphorus

    $CH_3PH_4 + 4O_2 \rightarrow CO_2 + 2H_2O + H_3PO_4 + \Delta H$
  - Methane Chloride

    $CH_3ClH_2 + 2O_2 \rightarrow CO_2 + H_2O + HCl + \Delta H$

Polymeric Plastic Combustion

- The combustion reaction takes place in the vapor phase
- 3 phases of products of pyrolysis:
  - Liquid
  - Solid
  - Vapor



Flame Retardant Families

Halogenated FRs

Chlorinated

- Wider Temperature range for radical release
- Used most commonly as a paraffin additive

Brominated

- Most common FR in production
- Five classifications, with over 75 compounds on the market
- High degree of control over release temperature

Halogenated FRs

- Act in the Vapor phase
- Reduce the heat generated by flames, thereby inhibiting the formation of flammable gases
- Behave according to a “Free Radical Trap” theory

Halogenated FR Mechanism

Free Radical Trap mechanism

$$R_n(Br)_x \xrightarrow{heat} R_n \cdot + Br \cdot$$

$$Br \cdot + H \cdot \rightarrow HBr - \Delta H$$

$$OH \cdot + HBr \rightarrow H_2O + Br \cdot$$

$$H \cdot + OH \cdot \rightarrow H_2O + \Delta H$$

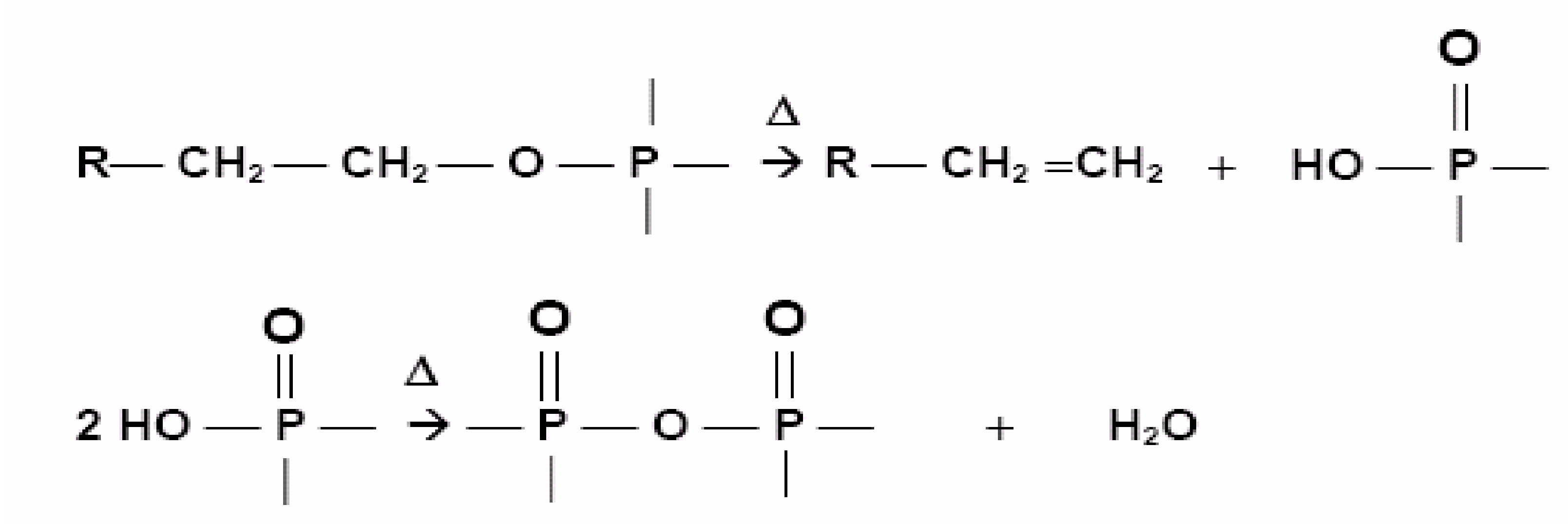
Process regenerates halogen radicals to perpetuate the reaction.

Phosphorus Containing FRs

- Additive to material it's protecting
- Acts in solid phase
  - Reacts to form phosphoric acid
  - Acid coats to form "char"
  - Char slows down pyrolysis step of combustion cycle

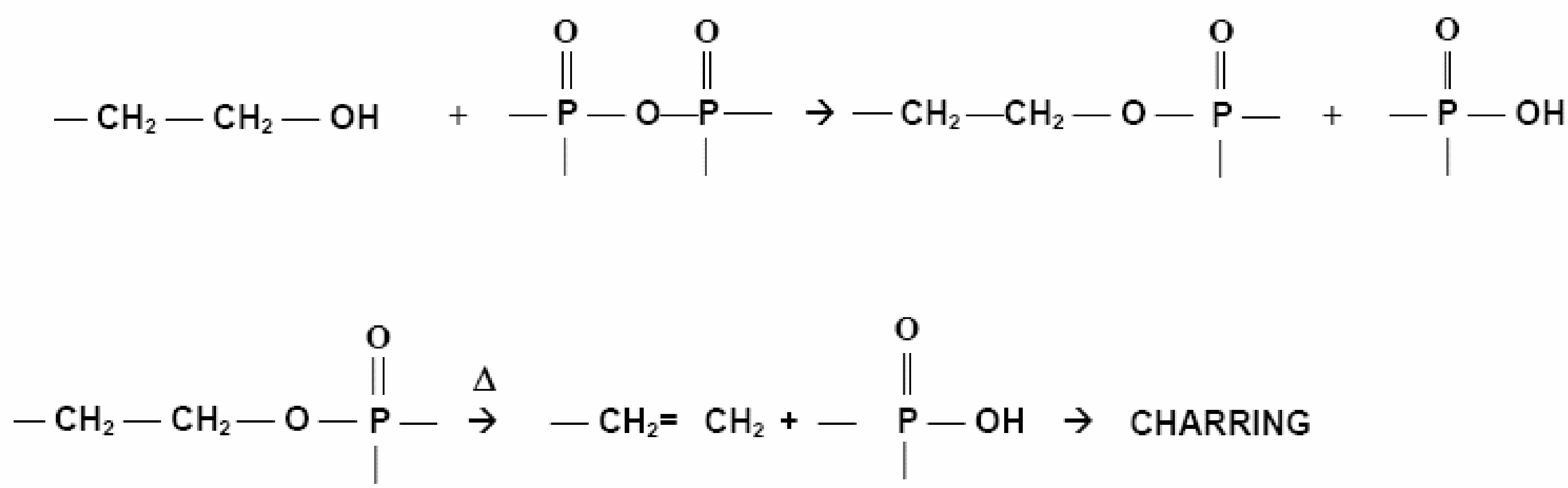
Phosphorus Containing FR Mechanism

- Thermal decomposition leads to the formation of phosphoric acid:



Phosphorus Containing FR Mechanism

- Phosphoric acid formed esterifies, dehydrates the oxygen-containing polymer and causes charring:



Phosphorus FR Pros

- Efficient FR Performance
- Needed Dosage Lower than Halogenated FRs
- Does Not Produce Toxic Smoke
- Does Not Produce Toxic Dioxins and Furans
  - described in more detail later

Phosphorus FR Cons

- Higher price/kg than Halogenated

- Have Limited Industrial Uses because of Mechanism
  - Char layer undesired in FR pajamas and similar products

Uses of Phosphorus Containing FRs

- Common Uses
  - Plasticizers
  - Plastics
  - Polyurethane Foam

Nitrogen Containing FR Mechanism

- Not a fully understood mechanism
- What is known:
  - Nitrogen gas is released into the atmosphere
    - Inert gas lowers the concentration of flammable vapors
  - Melamine transforms into cross-linked structures which promotes char formation
- Uses: Foams, Nylons and Polymers

Nitrogen FR Pros/Cons

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

Inorganic FRs

- Undergo decomposition reactions
- Release of water or non-flammable gases which dilute the gases feeding flames
- Adsorption of heat energy cools the fire
- Production of non-flammable, resistant layer on the material's surface
- Uses: PVC, Wires and Propylene

Common of Inorganic FRs

- Aluminum Hydroxide
- Magnesium Hydroxide
- Boron containing compounds
- Antimony Oxides
- Inorganic Phosphorus compounds

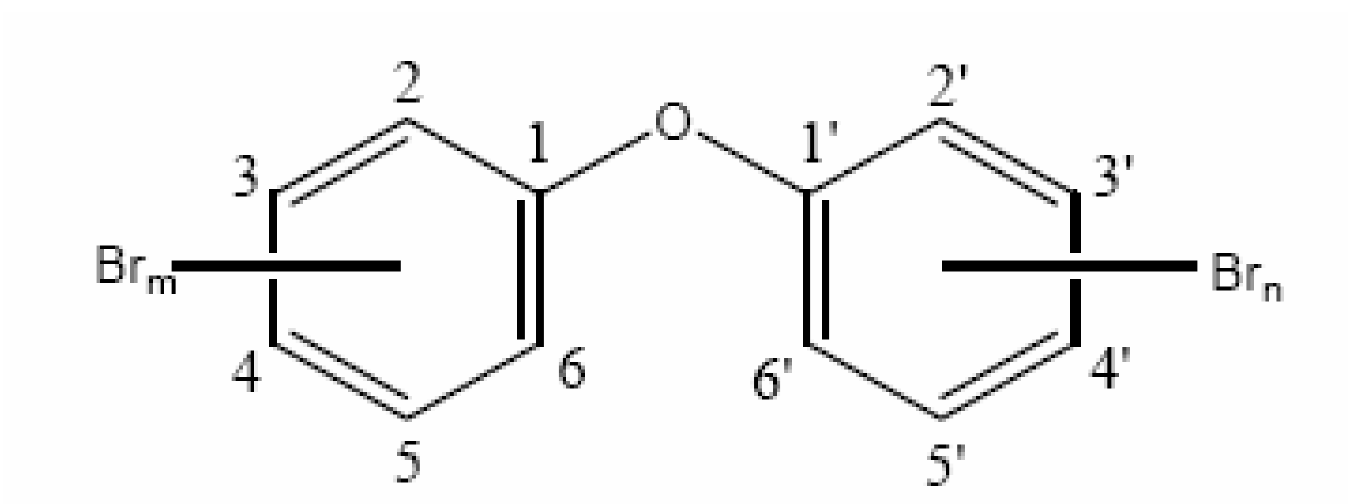
Inorganic FRs Pros/Cons

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

Problem Statement

Banned Chemicals

- Penta- and Octa-bromodiphenyl ether
- Where m + n = 5 for penta, =8 for octa



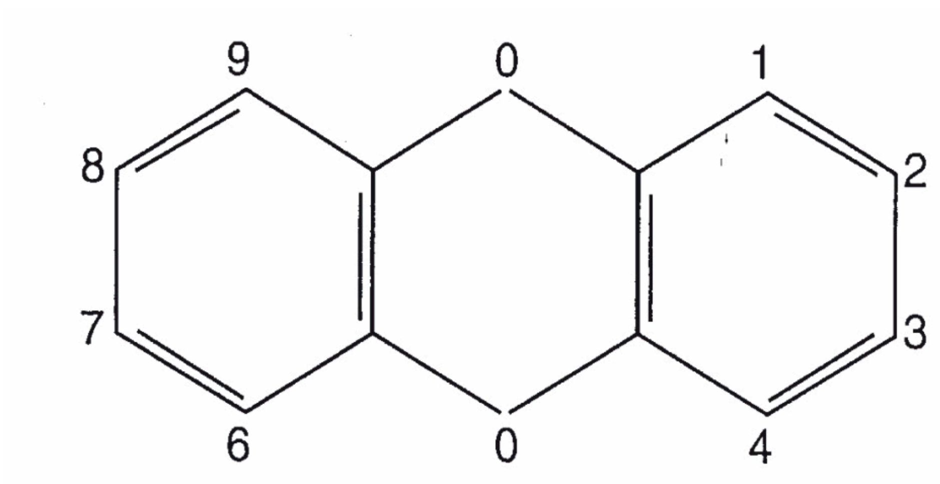
Banned Chemicals

- Penta- and Octa-bromodiphenyl ether banned in:
  - California by 2008
  - Europe as of next year
- Banned because of Environmental Concerns

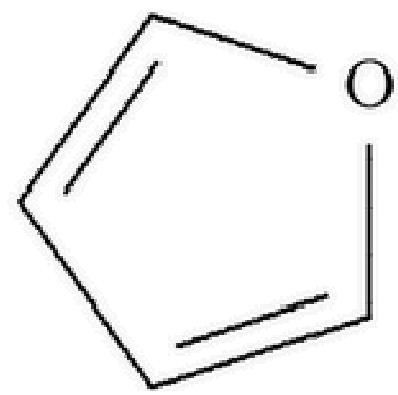
Environmental Concerns

- Ignition of brominated FR produces toxins found in soot
- Toxins have not been detected in fire’s gases
- No deaths have been documented to date
- Toxins are known as dioxins and furans

Toxins



Dioxin



Furan

Dioxin and Furan

- Unintentional by-product of many industrial processes
- Causes cancer in animals
- Causes severe reproductive and developmental problems
- Damages the immune system and interferes with hormonal systems
- Formed by burning halogen-based chemical compounds with hydrocarbons

Molecular Discovery

Molecular Discovery

- Molecular simulation involves using computer algorithms “derived from statistical mechanics to predict the properties of molecules and molecular assemblies”

- Models depend on intra- and inter-molecular interactions and computed group contributions (which come from published tables)

Molecular Discovery

- Desired Characteristics
  - Ease of ignition
  - Rate of Decomposition
  - Fuel contribution
  - Intensity of burning
  - Products of combustion

Molecular Discovery

- Group Contribution equations can be used to simulate relevant properties:
  - Auto-ignition Temp
  - Upper and Lower Flammability limits
  - Diffusivity in Air and Water
  - Vapor Density and Pressure
  - Normal Melting and Boiling Points
  - Gibbs Free Energy

Molecular Discovery

- Molecule simulation performed using excel spreadsheet
- Group contribution data were input from Perry's Handbook and Boethling & Mackay
- Calculated Boiling Point, Critical Constants, Enthalpies of Vaporization, and Fusion
  - These properties were used to determine flame retardant capabilities of each molecule

Molecular Discovery

- Determination of Phosphate Group Properties
  - Critical Constants for phosphoric acid from Pro-II
  - Using Excel spreadsheet and Pro-II data, solve for phosphate group contribution to T_{boil}, T_c, P_c, and V_c
  - We can now simulate properties for molecules containing the phosphate group

Discovery Process

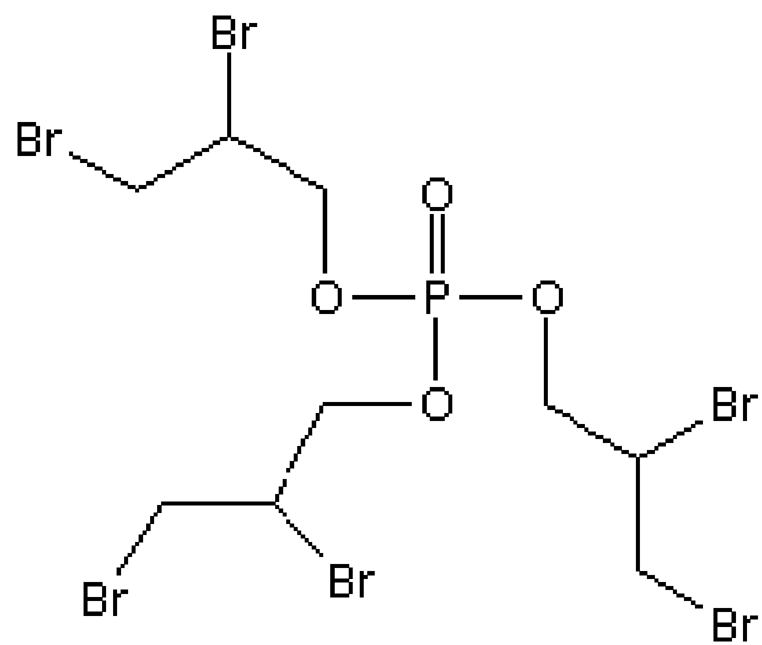
- Limitations of group contribution method will not allow for ideal molecule discovery
- Approach changed to simulation of known organic molecules containing phosphate **(LINK)**
  - Excluded aromatic molecules and transition metals based on desired properties of final product
  - Discarded molecules with BP lower than 513K
  - Ranked remaining four molecules according to vapor pressure at plastic melting point

Ranked Molecules & Properties

Rank	*Molecule*	T_C (K) eq 2-3	P_C (MPa) eq 2-7	V_C (m^3/kmol) Eq 2-14	(± 10 - 30%) Vapor P @ 513K (MPa)	(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	6.05×10^6	59.71×10^6

Tris(2,3-dibromopropyl) Phosphate

- Molecule simulated with strong performance indicators
- Structurally capable of retarding flames in both solid and vapor phases
- Unfortunately, already on the market as “Firemaster t23p” by the Great Lakes Chemical Co.

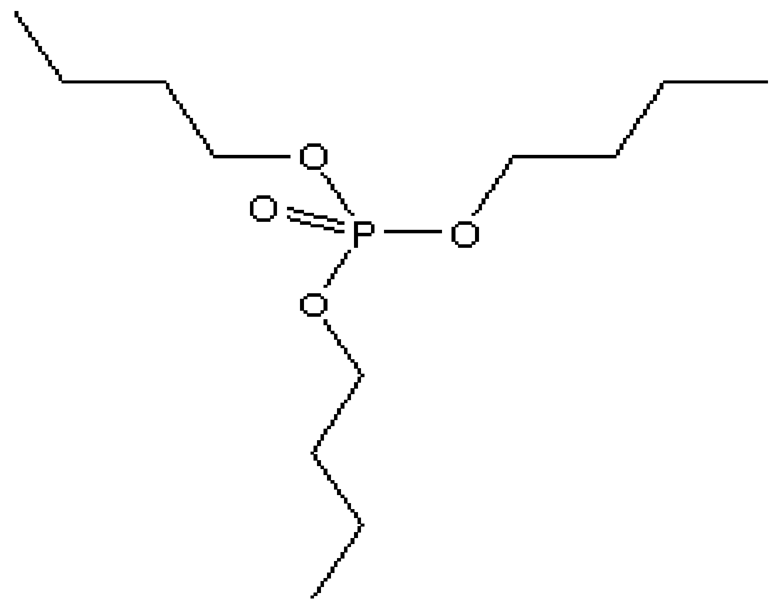


Properties of Tri-n-Butyl Phosphate

Flame-O 1000™

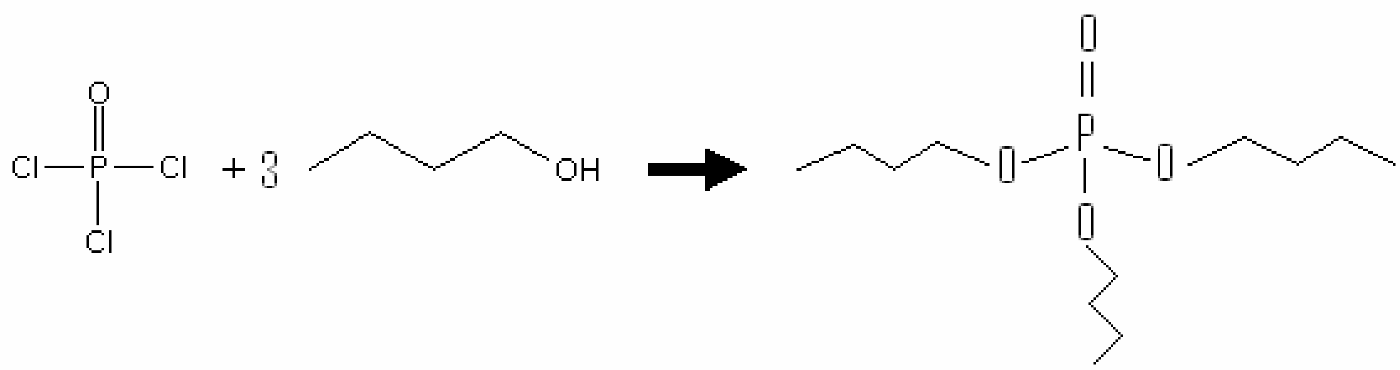
Flame-O 1000 ™ Properties

- Critical Temperature
  - 800K
- Critical Pressure
  - 1.38 MPa
- Critical Volume
  - 0.943 m^3/kmol
- Vapor Pressure @ 513K
  - 0.019 atm
- Boiling Point
  - 562K



Synthesis Path-Final

- Creation of Tri-n-Butyl Phosphate
  - N-butanol
  - Phosphoryl Chloride



Raw Materials

- N-butanol
  - Readily available
  - Can be purchased from a number of sources

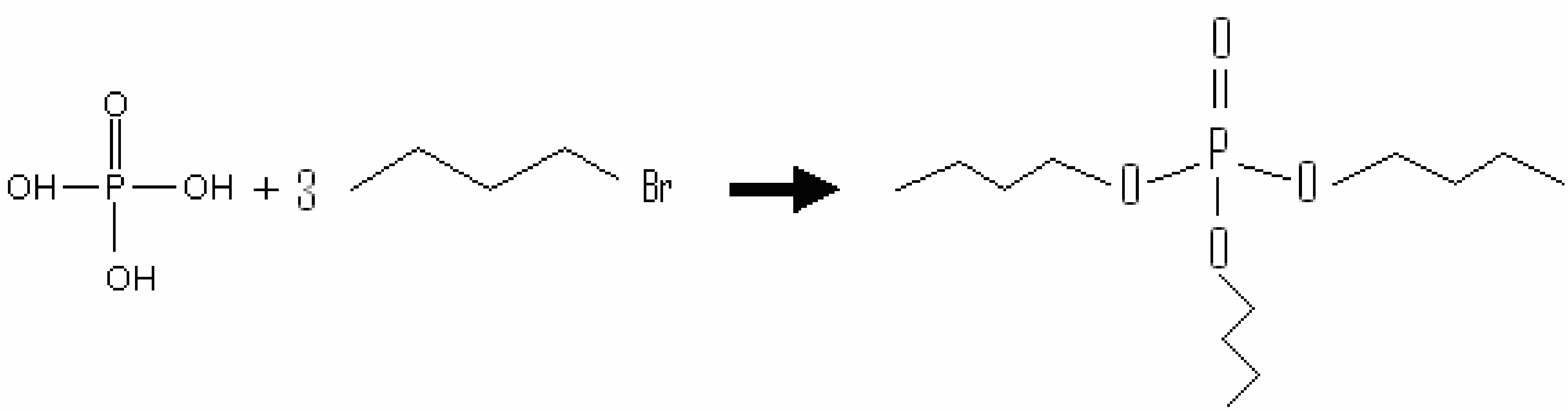
- Phosphoryl chloride
  - Less common
  - More expensive
  - Highly Reactive

Reasoning for Final Synthesis

- Occurs at room temperature due to high reactivity of phosphoryl chloride
- Occurs quickly due to high reactivity
- Occurs with a high conversion
- Should Test for the kinetics

Synthesis Path-Alternate

- Creation of Tri-n-Butyl Phosphate
  - 1-Bromobutane
  - Phosphoric Acid



Raw Materials

- 1-bromobutane
  - Readily Available
  - Relatively Cheap
- Phosphoric Acid
  - Readily Available
  - Relatively Cheap

Reasons Eliminated

- Requires heat for reaction to occur
- Slow reaction
- Low conversions

Testing

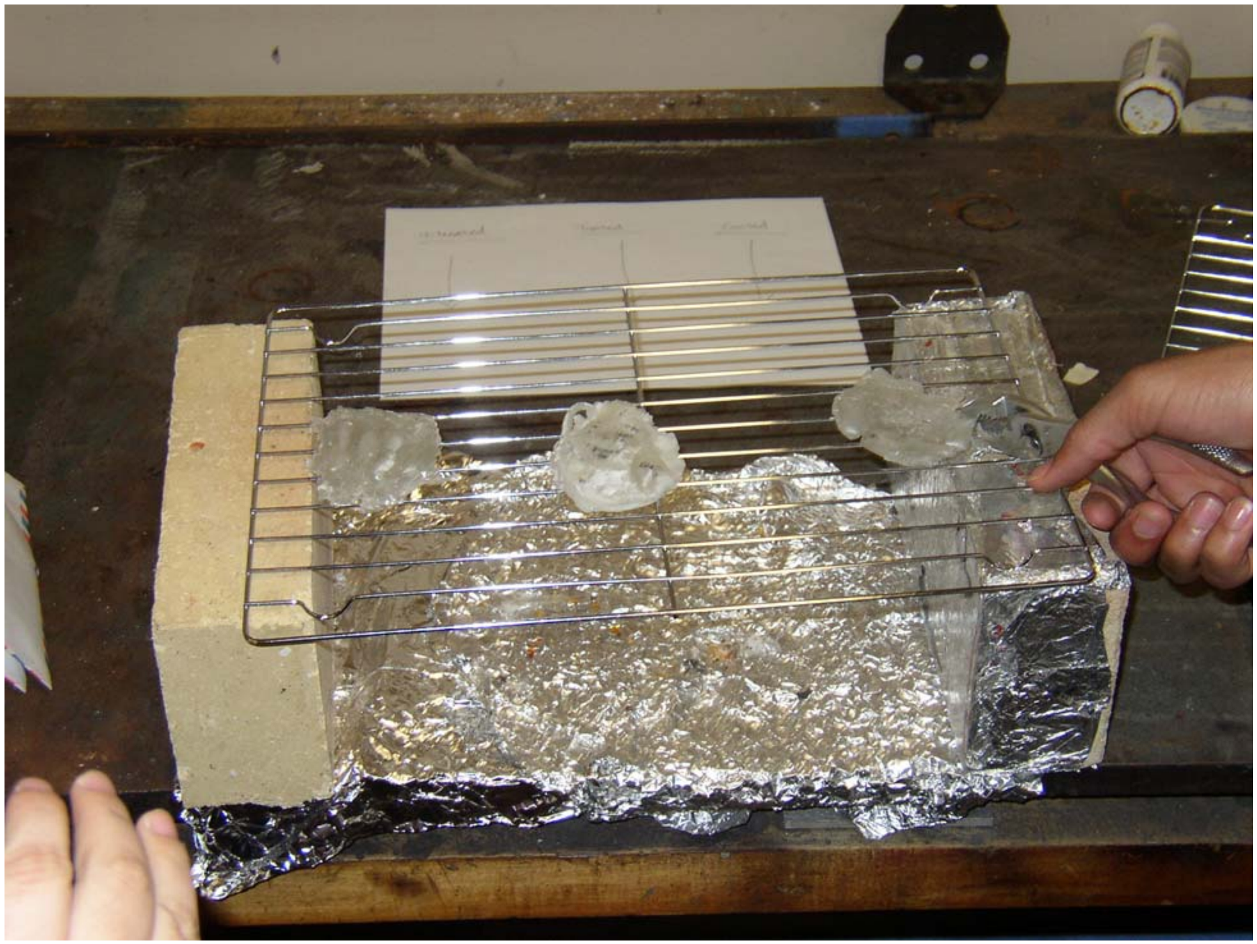
Tri-n-Butyl Phosphate Testing Materials

- Tri-n-Butyl Phosphate
- Polypropylene
- Metal Grills
- Acetylene Torch
- 2 Bricks
- Camera

Tri-n-Butyl Phosphate Testing Set Up

- Set up a horizontal metal grill with consistent and uniform flames provided below
- Flames should come from the side to prevent melted plastic from dripping on the burners
- Set-up mimicked 94 HB Horizontal Burn Test

Tri-n-Butyl Phosphate Testing Set Up



Tri-n-Butyl Phosphate Testing Procedure

- Prepare samples (10g total weight)
  - 1 as Standard
  - 1 as Coated
  - 1 as Additives
- Applied flames underneath keeping constant distance until samples ignited then removed flame
- Observe and document melting point and other characteristics of each sample

Tri-n-Butyl Phosphate Testing

Testing Results

Run		Untreated	Treated	Coated
2	Start Burning	11.5 s	14.6 s	14.5 s
	Go Out/Consumed	30.9 s	75.5 s	43.2 s
3	Start Burning	15.0 s	21.6 s	25.0 s
	Go Out/Consumed	30.5 s	67.7 s	53.6 s
4	Start Burning	--	21.4 s	23.4 s
	Go Out/Consumed	--	112.8 s	78.7 s

All times signify the time when it occurs, from zero

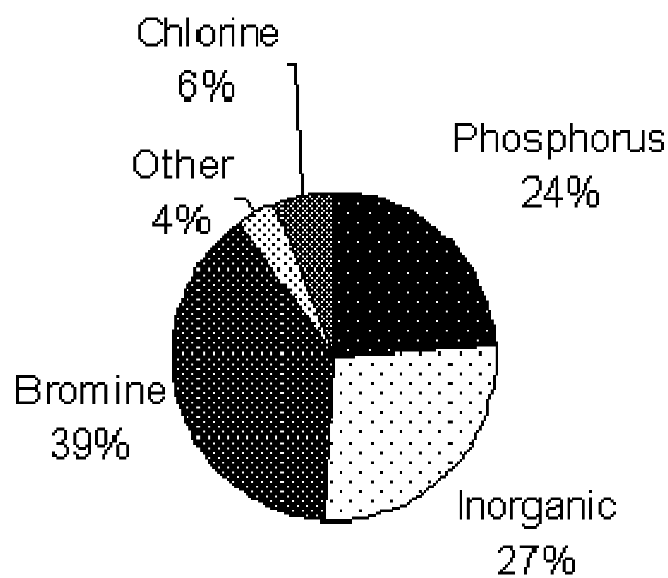
Testing Conclusions

- Noticeable difference between treated and untreated
  - At least twice as much time to catch fire and be fully consumed
- Coated samples produced the most smoke and overall performance was less effective than the treated samples
- Preferred method of applying Flame-O1000™ to plastic is as an internal additive as opposed to coating

The Market

World Market

- Global production: 2.2 billion pounds
- Global value: $2.1 billion
- As of 2002, the global market
  - 24% phosphorus
  - 27% inorganic
  - 6% chlorine
  - 39% bromine
  - 4% other



US Market

- 50% of the global market
- United States production:1.1 billion pounds
- United States value: $1.3 billion
- US breakdown is very similar in-group distribution to the global breakdown.

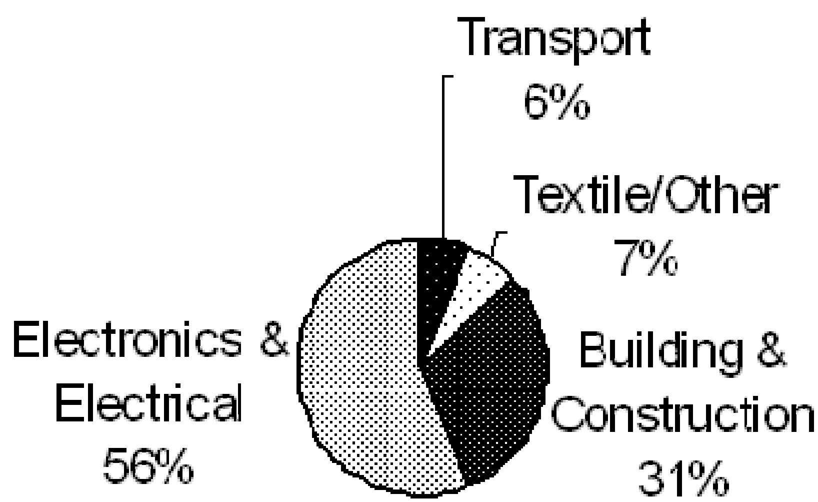
Brominated Market

- Major market contributor being phased out
  - Large void to fill

- Brominated FRs account for
  - Globally: $819 million
  - US: $507 million

Brominated Market

- Brominated FR Market Breakdown
  - Transport
  - Building and construction
  - Textile/other
  - Electrical & electronics



Phosphorus Market

- Phosphorus FRs account for
  - Globally: $504 million
  - US: $312 million

- Good market for our product to breach

Sellers

- Brominated
  - Great Lakes Chemical
  - Albemarle
  - Dead Sea Bromine Group
- Phosphorus
  - Great Lakes Chemical
  - Albemarle
  - Dow Chemicals

Market Status

- Demand to increase
  - Production:
    - Up 3.6% per year from 1.1 billion pounds in 2003
  - Value:
    - Grow 5.9% annually
  - Due to higher standards and higher use in industry
  - Due to specialty FRs that increase their share of the market

Market Status

- More items are being made from plastics
- Plastics reduce weight by eliminating:
  - Glass and metal
  - Lower production costs
  - Improving design and production flexibility
- Need for more FRs in specialized plastic FRs will increase as well.

Business Plan

Business Plan

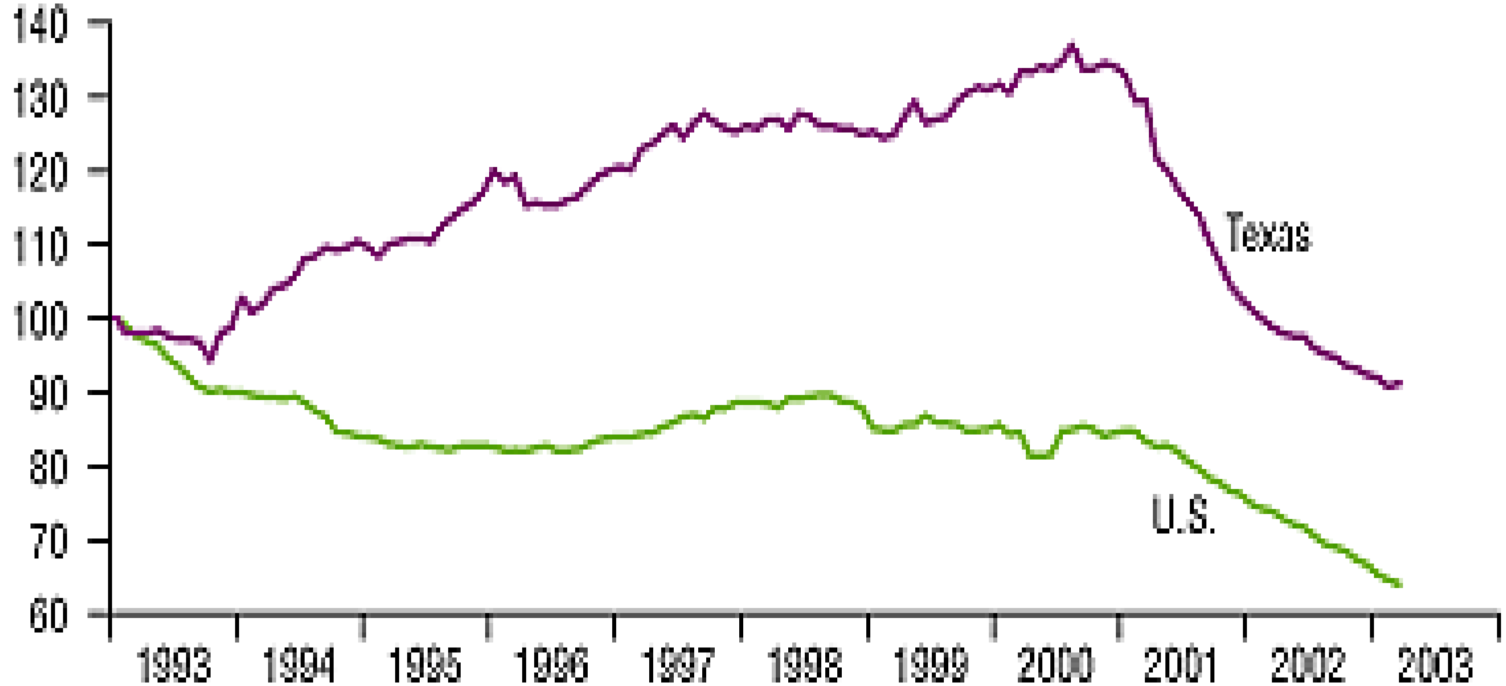
- Computers are cased in plastics
- Cost of computers are becoming cheaper
- Demand for computers is a necessity
- Computer market is growing
- KSM will target the computer industry

Potential Buyers

- Hewlett – Packard / Compaq
- Dell Computers
- IBM
- Apple

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.

Location

- Hewlett – Packard / Compaq
  - Based in Palo Alto, California
  - Compaq based in Houston, Texas
  - Responsible for 44% of Texas computer employment
- Dell Computers
  - Based in Austin, Texas
  - Responsible for 52% of Texas computer employment

Target Company

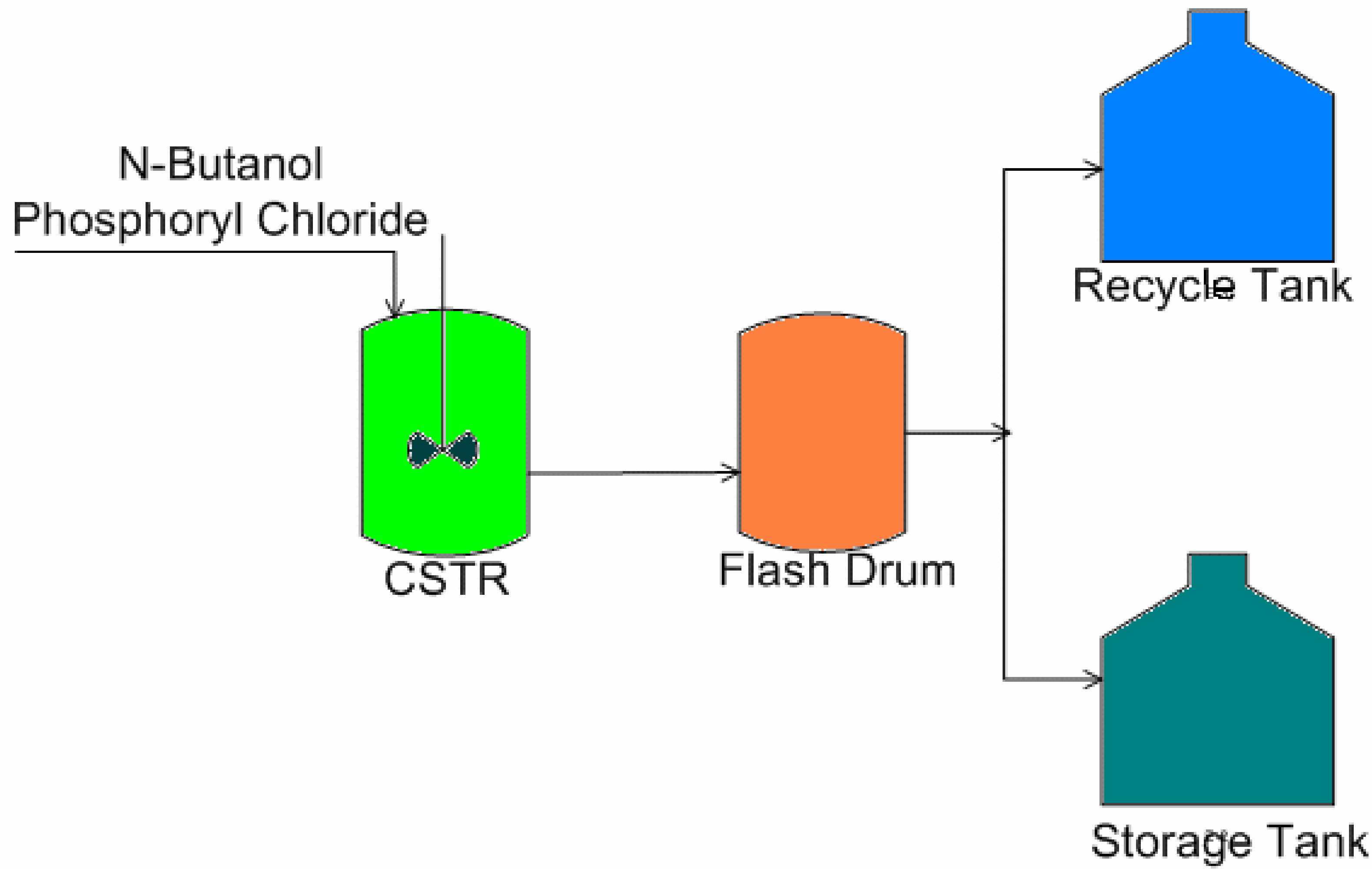
- Dell Computers
  - Major Contributor to Computer Sales
  - Sell a Variety of Electronic Devices
    - Desk Top Computers
    - Lap Top Computers
    - MP3 Players
  - Convenient Plant Location

Investment Opportunity

- Initial Investment
  - $4 Million to license the chemical modeling of Flame-O 1000™
- Plant Addition will be constructed in six months
- Start construction with initial payment

Economics of Plant Design

Flow diagram



Cost of equipment

	$V_{Batch\ Reactor}$ m3	$	$V_{flash\ Drum}$ m^3	$	Storage tank (500m3)	Total equipment cost
1	3.13	$38,802	3.13	$23,500	$ 118,662	$ 180,964
2	3.79	$42,936	3.79	$24,000	$ 125,185	$ 192,121
3	5.71	$53,333	5.71	$25,300	$ 131,708	$210,341
4	7.00	$59,403	7.00	$25,900	$ 138,231	$ 223,534
5	8.22	$64,673	8.22	$26,400	$ 144,754	$ 235,827
6	10.34	$73,021	10.34	$37,100	$ 151,277	$ 261,398
7	14.10	$86,043	14.10	$40,100	$ 157,800	$ 283,943

Cost of Raw Materials

	Product (TBP) mi kg/yr	n-Butanol mi kg/yr	POCl3 mi kg/yr	Total cost
1	1.11	1.16	0.80	$2,327,260
2	1.23	1.28	0.88	$2,578,856
3	1.54	1.61	1.11	$3,228,811
4	1.70	1.77	1.22	$3,564,272
5	1.85	1.93	1.33	$3,878,767
6	2.09	2.18	1.51	$4,381,958
7	2.50	2.61	1.80	$5,241,577

Economic

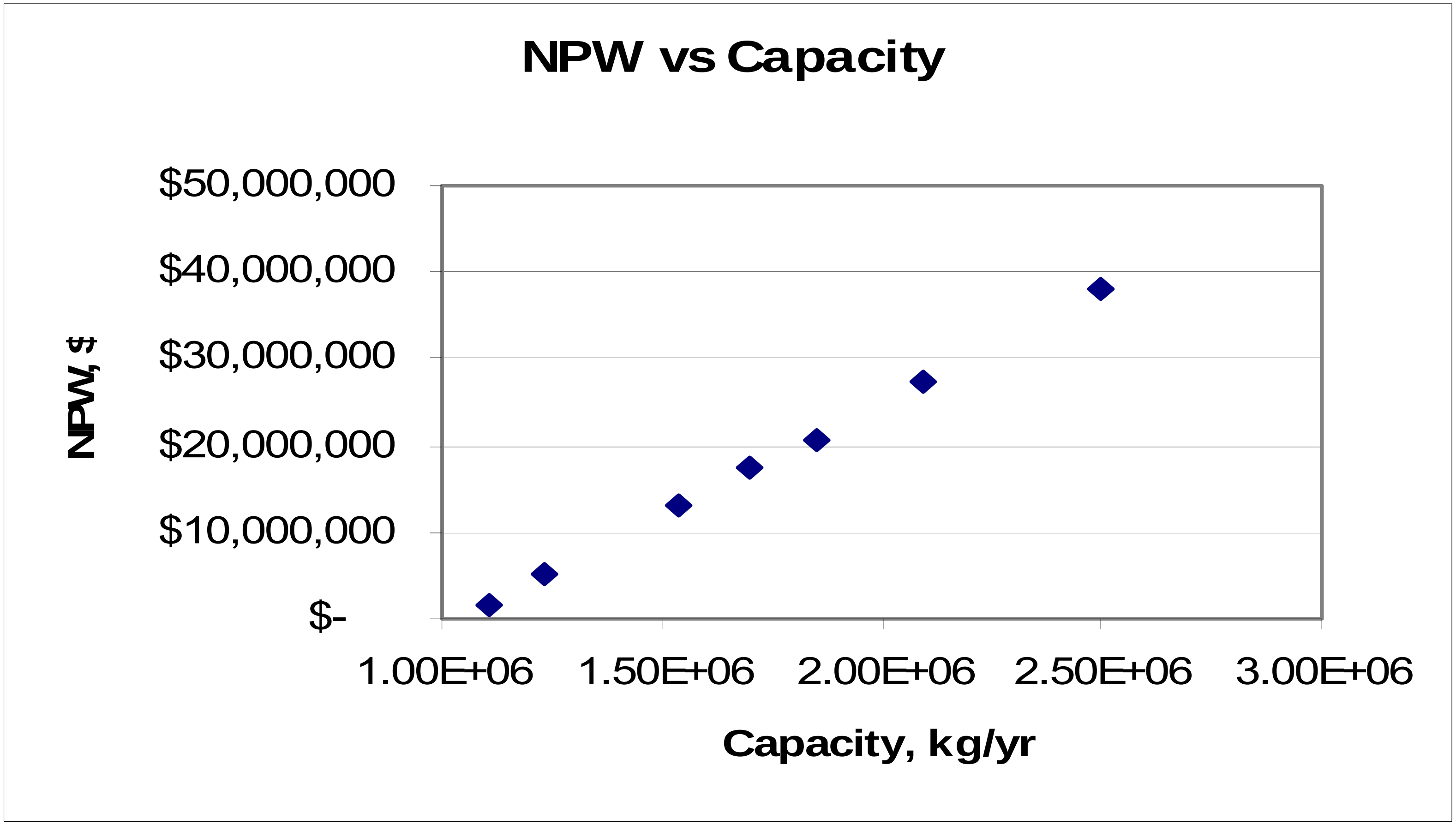
- Product cost: $10/kg
- Operating labor: 3-6workers/ 3shifts/ day
  - Labor cost: $15/hr
- Utility cost: electricity cost for Reactor and Flash Drum based on PRO II simulation
- Project plan: 10 year period

Economic

	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

Includes licensing fee

Net Present Worth vs. Capacity



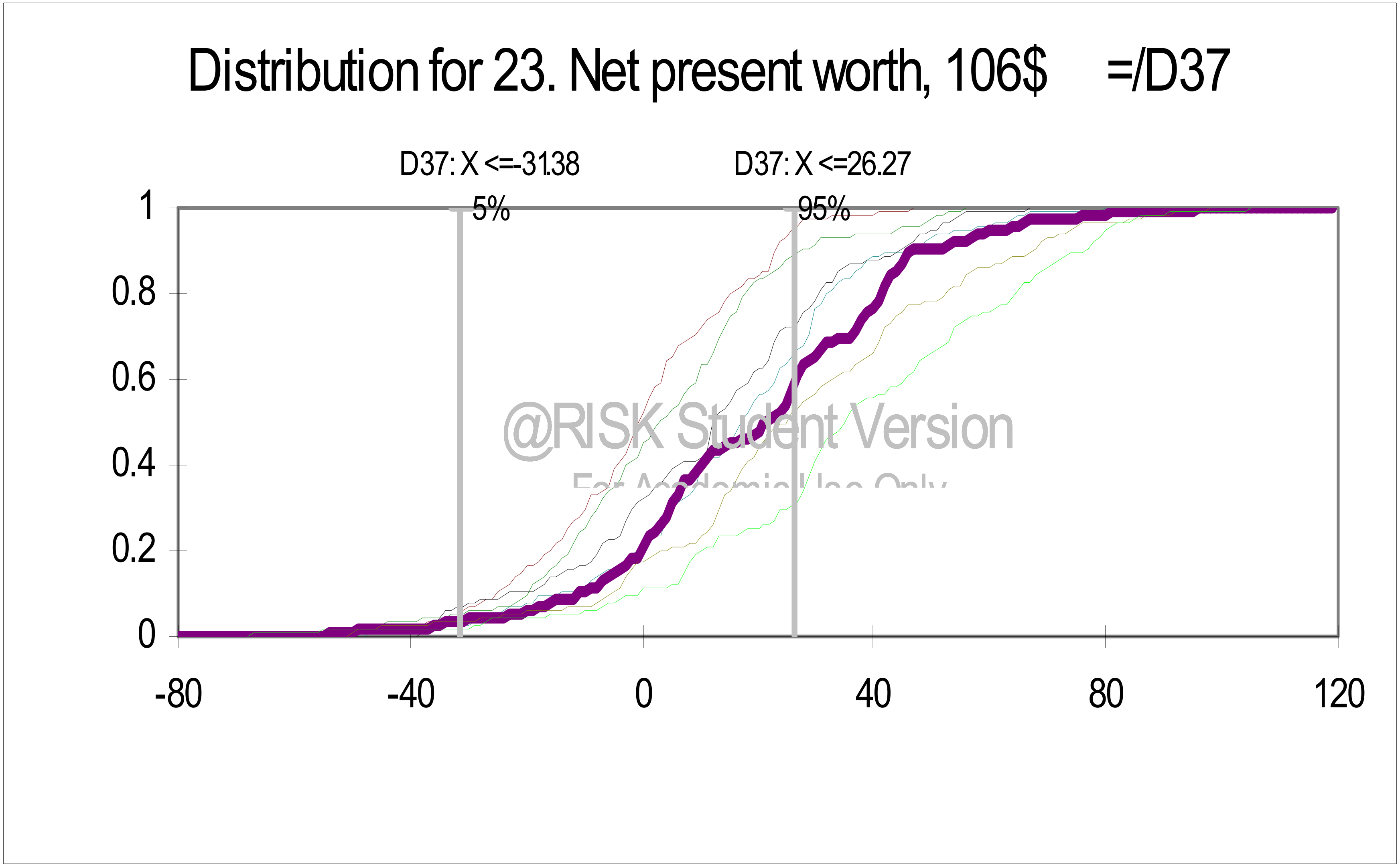
Risk Analysis

- Base capacity of 1,230,000 kgs/yr was proposed
- The capacity was picked by:
  - Taking the available US market (1.1 billion pounds)
  - Multiplying by 39%
    - wt% brominated FRs
  - Multiplied by 20%
    - assumed fraction missing due to the ban/phase out
  - Multiplied by 3.5%
    - fraction of the market our product will replace

Risk Analysis

- Product-selling price was $10/kg
  - Based on Great Lakes Chemical's average phosphorus price of $12/kg
- Capacity range:
  - 1,110,000 to 2,500,000 kg/year
- Base standard deviation of 40% for:
  - Capacity
  - Product price
- Net present worth (NPW) was exported to create risk curves, seven risk curves were made

Risk Curve


Distribution for 23. Net present worth, 106$ =/D37
D37: X <=-31.38
5%
D37: X <=26.27
95%
1
0.8
0.6
0.4
0.2
0
-80
-40
0
40
80
120
@RISK Student Version

Economic

- Risk curve #5 was chosen
- Capacity: 1.85 million kg/yr
- NPW: $20,700,000
- ROI: 87%

Questions