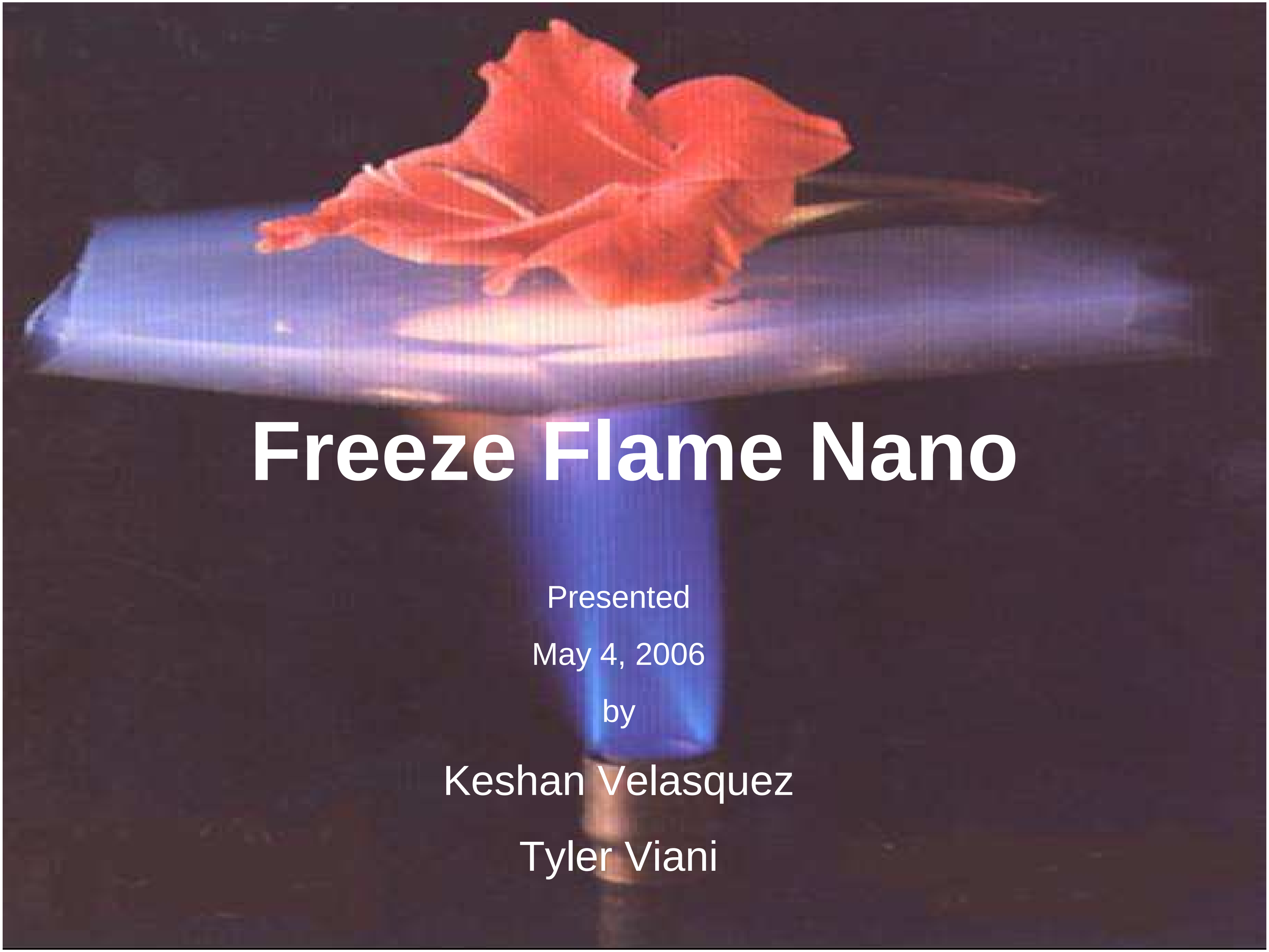

Freeze Flame Nano

Presented

May 4, 2006

by

Keshan Velasquez

Tyler Viani

Outline

- Introduction to Fires and Flame retardants
- Problem Statement
- Product Discovery
- Economics and Business Plan
- Conclusions and Recommendations

How a Fire Starts[1]

- Material comes in contact with heat source
- Pyrolysis – Decomposition of material
- Flammable gas reacts with oxygen
- H· and OH· radicals are released

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[1] *How Flame Retardants Work?* EFRA. Accessed January 2006. <http://www.cefic-efra.com/>

Importance of Flame Retardants[2]

- 1.7 million fires annually from 1995-2004
  - 500,000 occurred in building structures
- 4,000 civilian fire deaths
- 21,000 civilian fire injuries

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[2] United States Fire Administration. *National Fire Statistics*. Accessed January 2006. www.usfa.fema.gov/statistic/national/

Goal of Flame Retardants

- Increase resistance to ignition of fire
- Delay the spread of flame providing time for either extinguishing the flames or for escaping
- Save lives

Flame Retardant Families[1]

- Halogenated
  - Most often bromine
    - Less electronegative / weaker bonds
  - Remove H· and OH· radicals

  - Relatively low cost
  - Potentially toxic
  - Not biodegradable

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[1] *How Flame Retardants Work?* EFRA. Accessed January 2006. <http://www.cefic-efra.com/>

Flame Retardant Families[1]

- Phosphorus
  - When heated, H_3PO_4 is released causing charring
  - Char layer protects material from heat
  - Nontoxic, biodegradable
  - Lower concentrations can be used
  - Higher price than halogenated

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[1] *How Flame Retardants Work?* EFRA. Accessed January 2006. <http://www.cefic-efra.com/>

Flame Retardant Families[1]

- Nitrogen
  - Nitrogen gas dilutes flammable gas
  - Cross-linked structures inhibit pyrolysis

  - Can partially replace other flame retardants
  - Must be used in high concentrations or in conjunction with another flame retardant
  - Mechanism not fully understood

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[1] *How Flame Retardants Work?* EFRA. Accessed January 2006. <http://www.cefic-efra.com/>

Flame Retardant Families[1]

- Inorganic
  - Aluminum Hydroxide / Magnesium Hydroxide
    - Endothermic reaction
    - Forms protective layer and dilutes gases in air.
  - Boron Compounds
    - Form protective layer, causes charring

  - Easily incorporated into plastics
  - High concentrations needed

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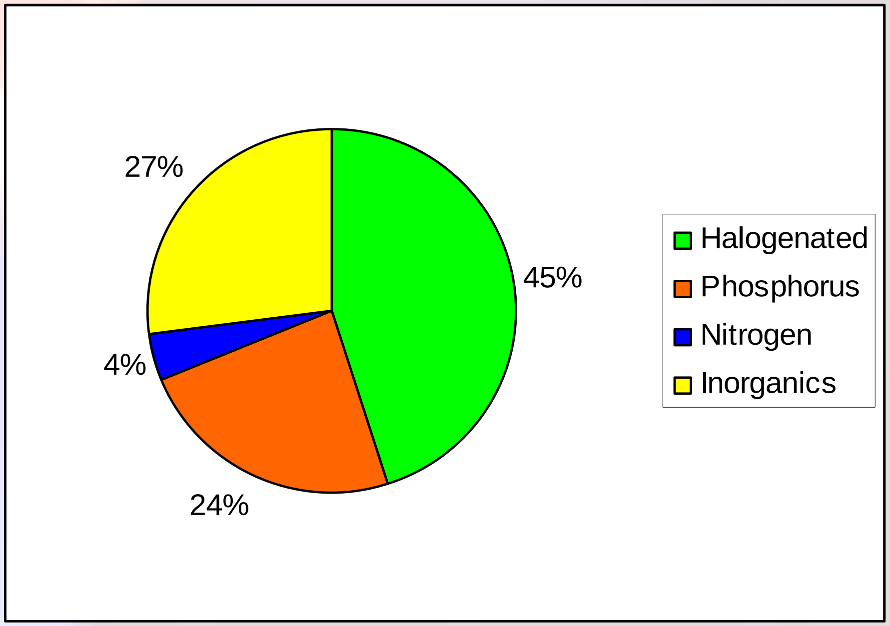
[1] *How Flame Retardants Work?* EFRA. Accessed January 2006. <http://www.cefic-efra.com/>

Flame Retardant Market[3]

- Market as of 2006
  - Globally
    - 2 billion pounds
    - $2.1 billion
  - U.S.
    - 1 billion pounds
    - $1 billion
  - Flame Retardant Coatings
    - 24.5 million pounds
    - $27.6 million



[3] Lerner, Ivan. "FR Market Down but Not Out: Albemarle Stays the Course." *Chemical Market Reporter*. December 10, 2001 p. 12.

Market Projections[3]

- Demand for Flame Retardants to grow 3.6% annually
- Market Value to increase 5.9%

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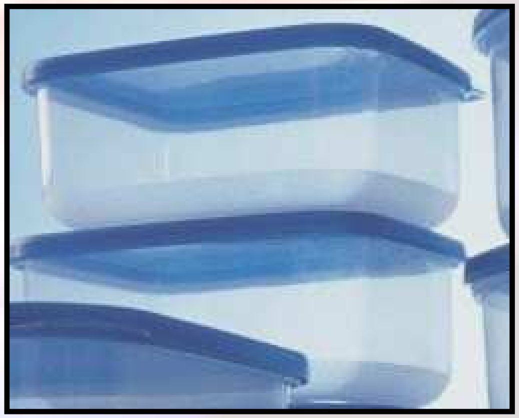
[3] Lerner, Ivan. "FR Market Down but Not Out: Albemarle Stays the Course." *Chemical Market Reporter*. December 10, 2001 p. 12.

Problem Statement

- Develop a biodegradable, non-toxic flame retardant and analyze economic feasibility

Flame Retardant Development

- Product options
  - Impregnation
    - Plastics and rubbers
  - Coating
    - Wood
    - Some plastics
  - Filler
    - Insulation
  - Outdoor Treatment
    - Shingles/Sheds



Flame Retardant Development

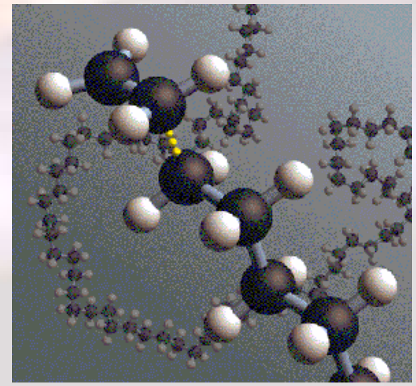
- Our product: Flame-retardant polymer coating (thermoplastic)
- Proposed Applications
  - Construction (Predominately)
  - Plastics (Some)
  - Electronics (Some)

Flame Retardant Development

- Polymer Properties
  - High heat resistance
  - Increase retarding time (char inducing)
  - Multiple applications
  - Cheap

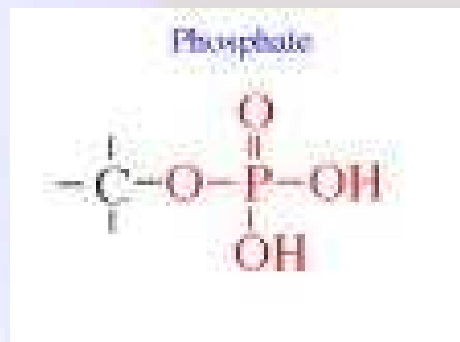
Flame Retardant Development

- Required Raw Materials
  - Polymer
    - Water Soluble
    - Biodegradable
  - Clay (nano)
  - Phosphate
  - Water
- Preferred Raw Materials
  - Polyvinyl Alcohol (PVOH)
  - Cloisite
  - Phosphate

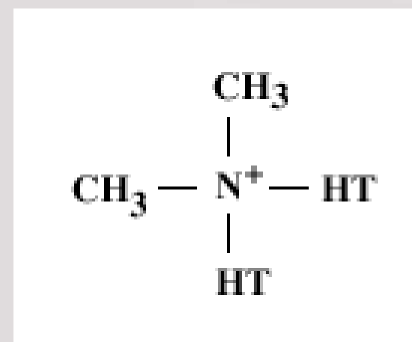


Polymer

+



Phosphate



Nano-clay

(Cloisite)

↓

Flame Retardant

Why Use PVOH?

- Polyvinyl alcohol
  - Made from saponification of PVAc
  - Uses
    - Adhesives
    - Emulsion paints
  - Biodegradable
  - Very polar

Why Use Nano-Clay?

- Cloisite* (Montmorillonite family)
  - Properties exhibited
    - Increased elasticity modulus
    - Elevated heat distortion temperature
    - Enhanced flame retardant properties
    - Good recycling properties
    - Easily dyed
    - Tends to align parallel to polymer substrate

---

*http://www.users.bigpond.com/jim.chambers/Cloisite.htm

Why Use Phosphates?

- Phosphates (RH_2PO_4, R=Alkyl group)
  - Relatively inexpensive
  - Can exist in nature (not harmful)
  - Induces high levels of char
    - Stabilizes pyrolysis reactions
    - Distributes heat evenly
    - Decreases heat conduction

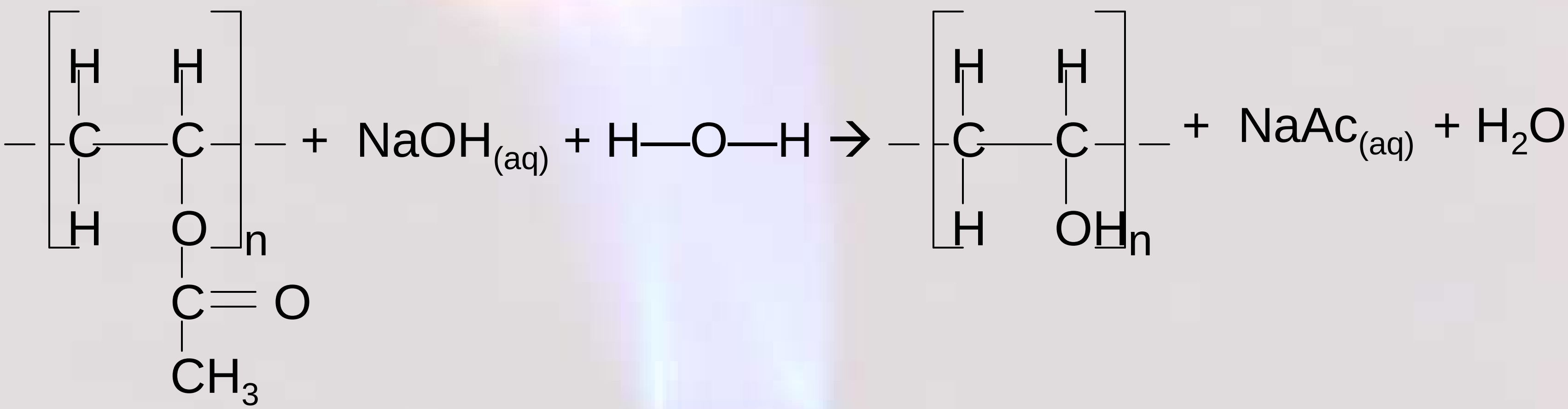
Uses in Industry

- Thermosets
  - Reentry cones, fuel tanks and engine encasings
- Thermoplastics
  - Wires, cables, flooring, conveyor belts, tubing, etc.
- GM
  - Cargo beds and auto exterior

Flame Retardant Development

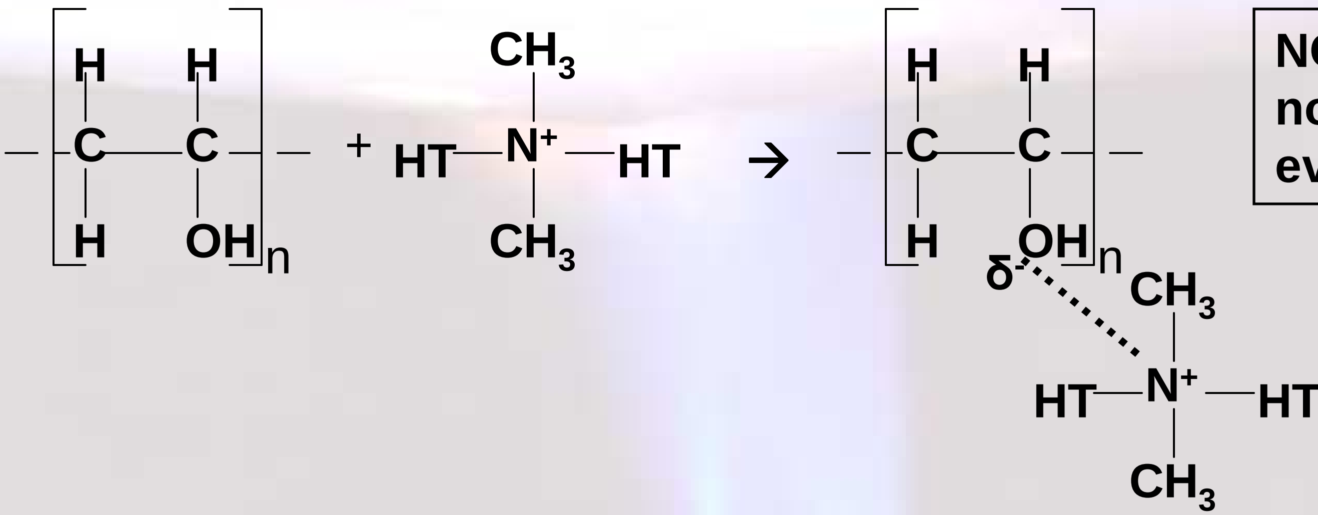
- Synthesis Path (Saponification of PVAc)

$$PVAc + NaOH_{(aq)} + H_2O \rightarrow PVOH_{(aq)} + NaAc_{(aq)} + H_2O$$



Flame Retardant Development

- Synthesis Path (Mixing)

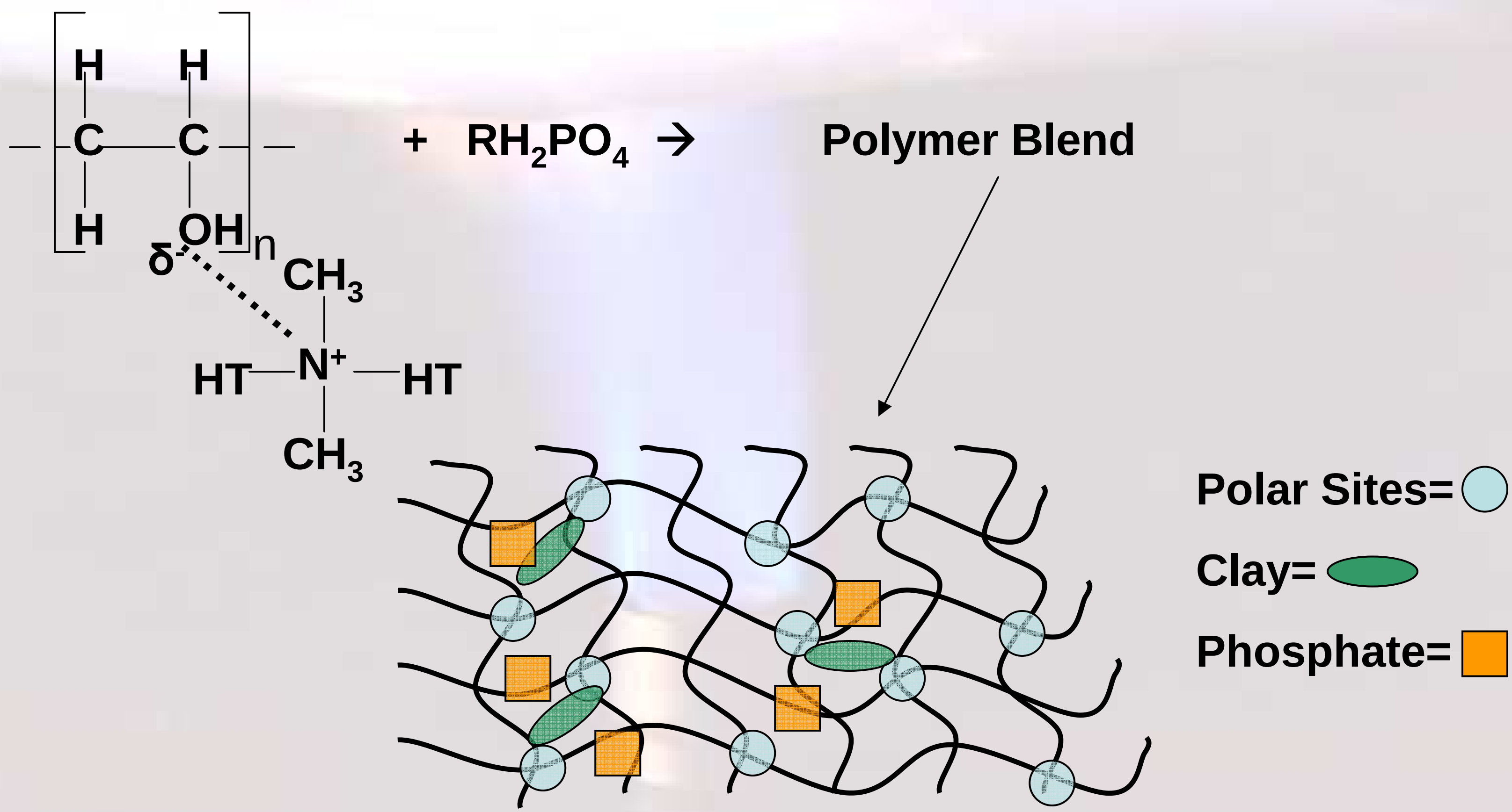


NOTE: This will not occur at every OH-site

Polymer Slurry:

Flame Retardant Development

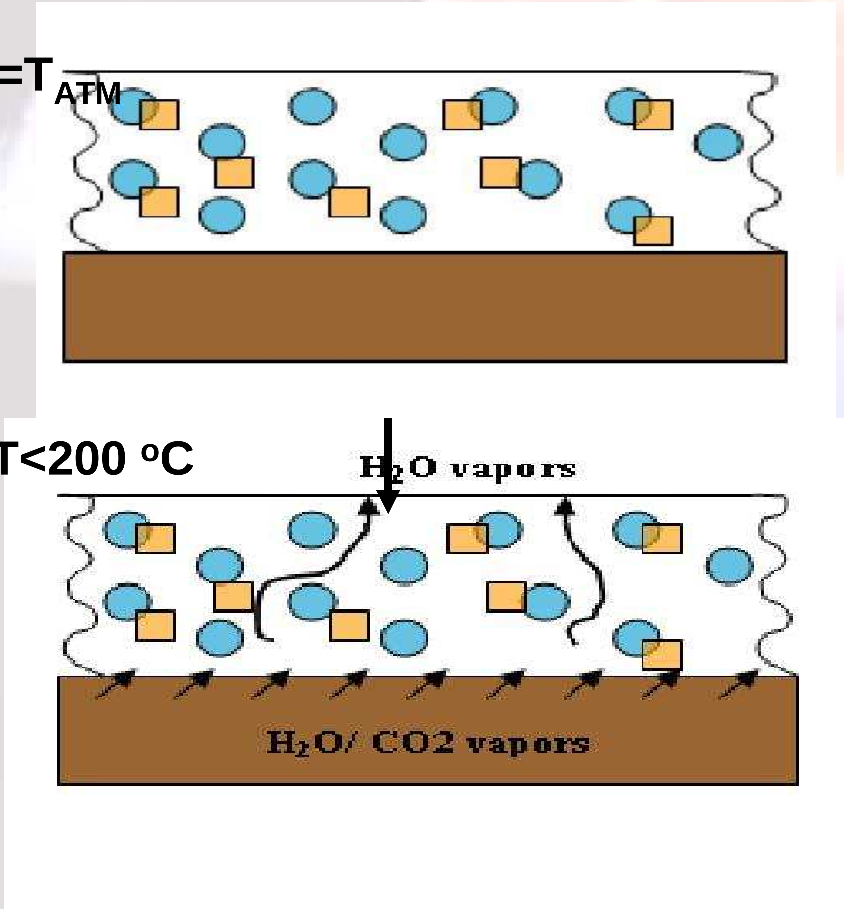
- Synthesis Path (Extruding)



Method of Action[6]

$T=T_{ATM}$

$T<200\ ^oC$



Pyrolysis

- **Wood dehydrates**
- **Water vapors and trace carbon dioxide released**
- **Small amounts of formic and acetic acid vapors**

Combustion

- **Slight oxidation reactions occur on wood surface**
- **Slow but steady loss of weight**
- **Trace non-ignitable gasses released**

Key

○ = **Cloisite**

□ = **Phosphate**

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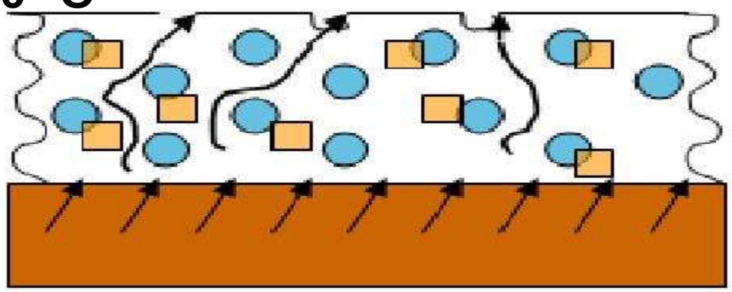
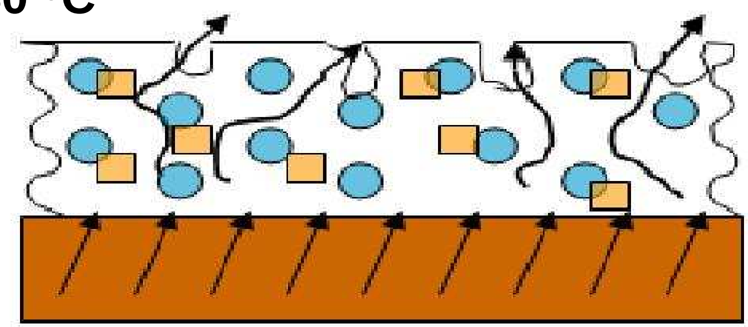
[6] Browne, F.L. *Theories of the Combustion of Wood and Its Control. A Survey of the Literature. Forest Products Laboratory, Forest Service U.S. Department of Agriculture.*

Method of Action

T=200 ^{o}C



T<280 ^{o}C



Pyrolysis

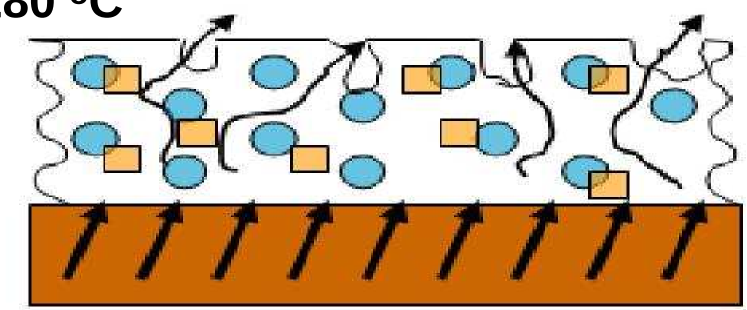
- Slow endothermic pyrolysis reactions continue
- Toxic carbon monoxide begins diffusing
- Minor surface charring

Combustion

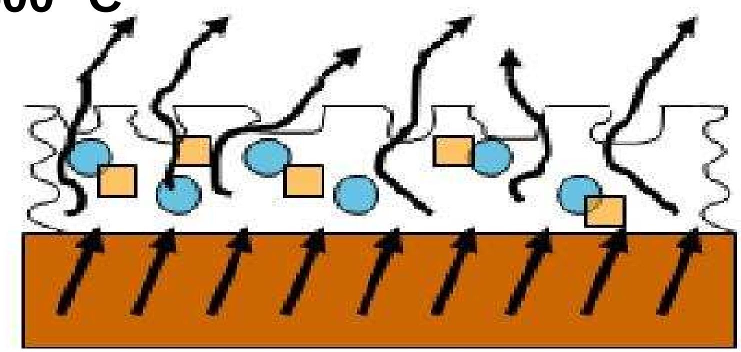
- Exothermic temperature reached (~240 ^{o}C)
- Ignitable gasses emitted
- Larger temperature gradient within the wood

Method of Action

T=280 ^{o}C



T<500 ^{o}C



Pyrolysis

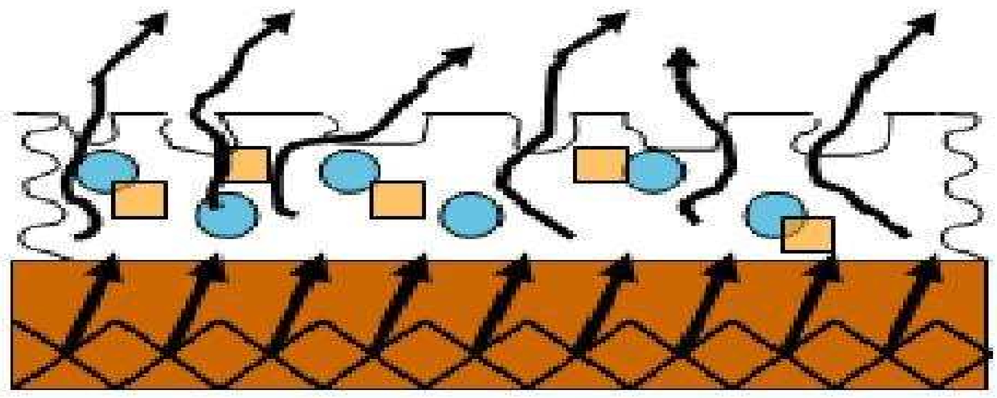
- Onset of exothermic pyrolysis
- Vapors eject tars that appear as smoke
- “Smoking” persists until T~400 ^{o}C

Combustion

- Secondary pyrolysis results in vapor combustion
- Gasses rapidly emerge
- Char layer develops quickly around T=400 ^{o}C

Method of Action

T>500 ^{o}C



<u>**Pyrolysis**</u>

- **Maximum surface temperature reached**
- **Vigorous secondary reactions complete carbonization process**
- **Tars and gaseous byproducts are further pyrolyzed into more combustible products**

<u>**Combustion**</u>

- **Surface temperature rise resulting from exothermic rxns.**
- **Wood glows as carbon is consumed**
- **Primary/secondary reactions cease → smoldering ember remains**

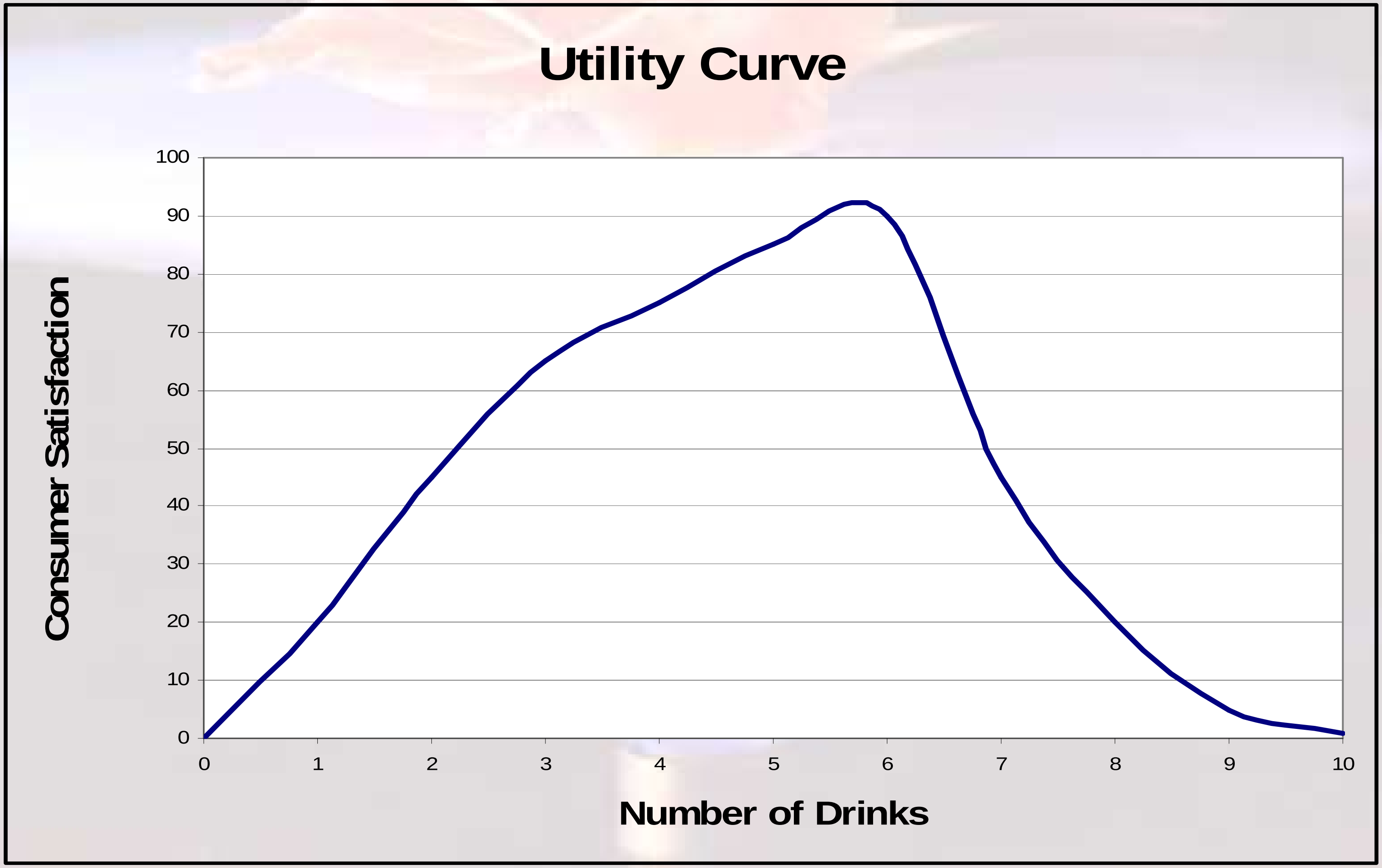
Flame Retardant Development

- Producer considerations
  - High thermal resistance
  - Low volatility
  - Low vapor pressures
  - Overall versatility
  - Competitive cost
- Consumer considerations
  - Retardancy time
  - Number of applications
  - Odor
  - Setting time
  - Effective amount

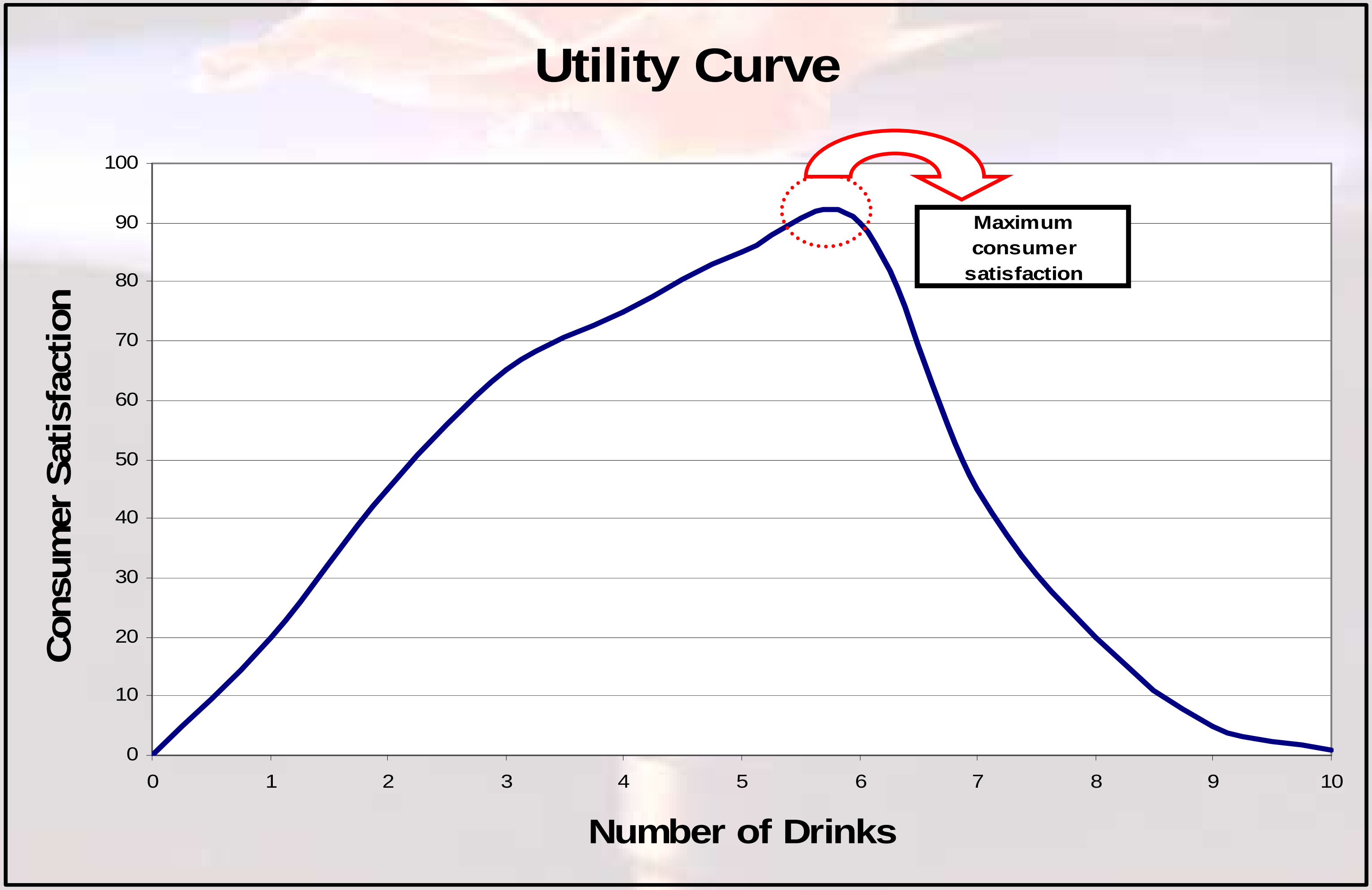
Consumers and Utility

- Utility
  - A measure of the happiness or satisfaction gained from consuming a good or a service
  - Attempt to always maximize utility in products
- Product development
  - Utility measurements provide means to enhance a products' appeal (demand) to the consumer
  - Maximizing utility generates a products maximum happiness
  - Generate a product "happiness function" that attempts to maximize utility (happiness)

Consumers and Utility



Consumers and Utility



Consumer Happiness

- Happiness function
  - Relate consumer attributes to product happiness
    - Assign scores corresponding to consumer attributes
    - Normalize scores on a 0-1 scale

    Ex: Let 1-scoop of ice cream → 50% happy (0.50)

    2-scoops of ice cream → 75% happy (0.75)
  - Relate consumer attributes to a quantifiable physical property

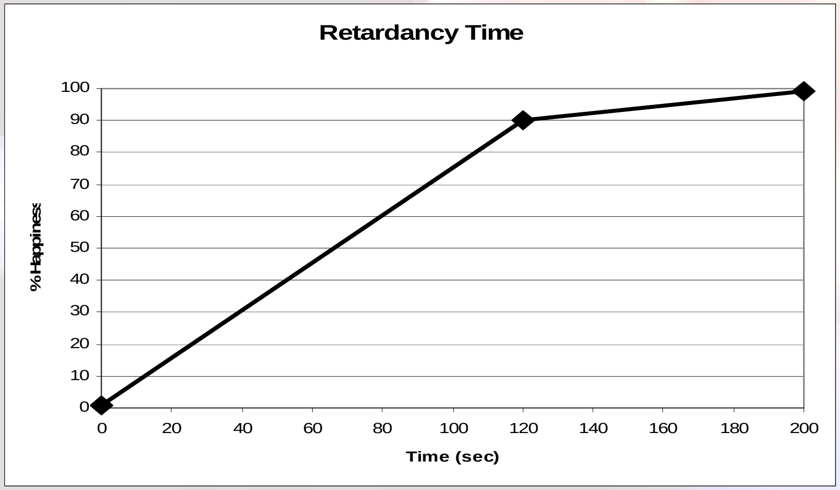
    Ex: Measure, 1-scoop = 0.50 wt% sucrose ($C_{12}H_{22}O_{11}$)

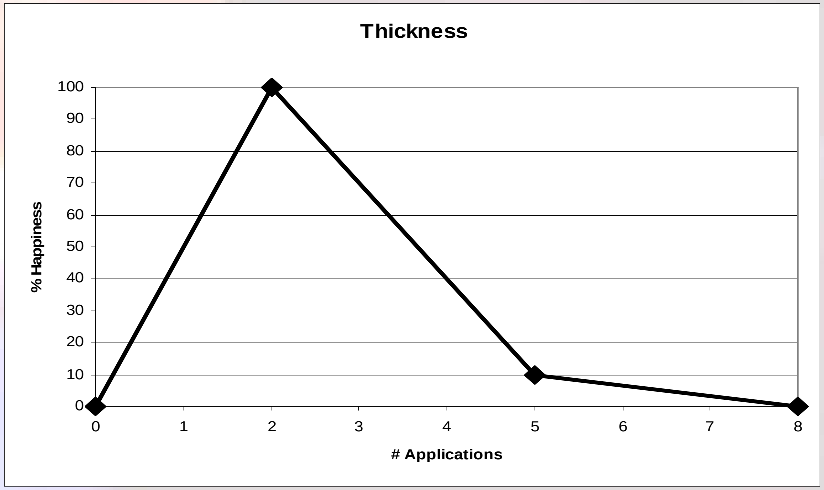
    2-scoop = 1.00 wt% sucrose ($C_{12}H_{22}O_{11}$)

Consumer Happiness

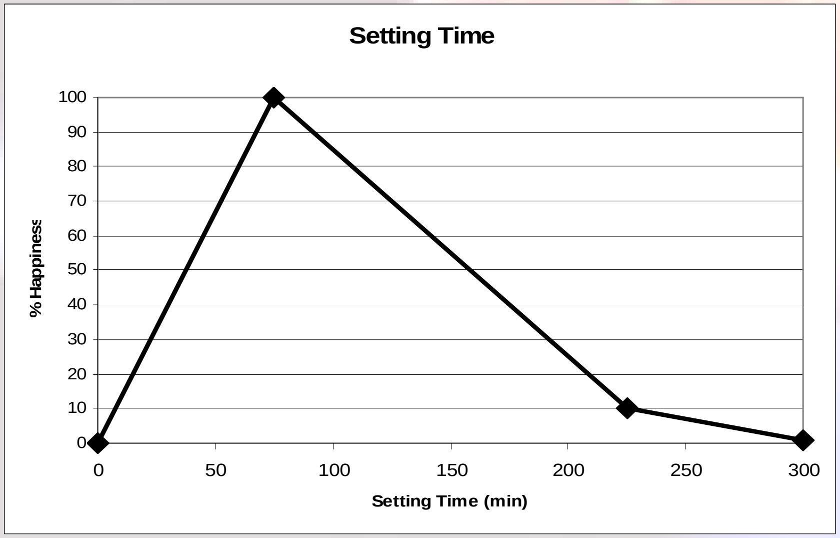
- Happiness function (cont'd)
  - Altering sucrose concentrations changes the amount in each "scoop"
  - Overall consumer happiness changes resulting from changes in sugar concentrations

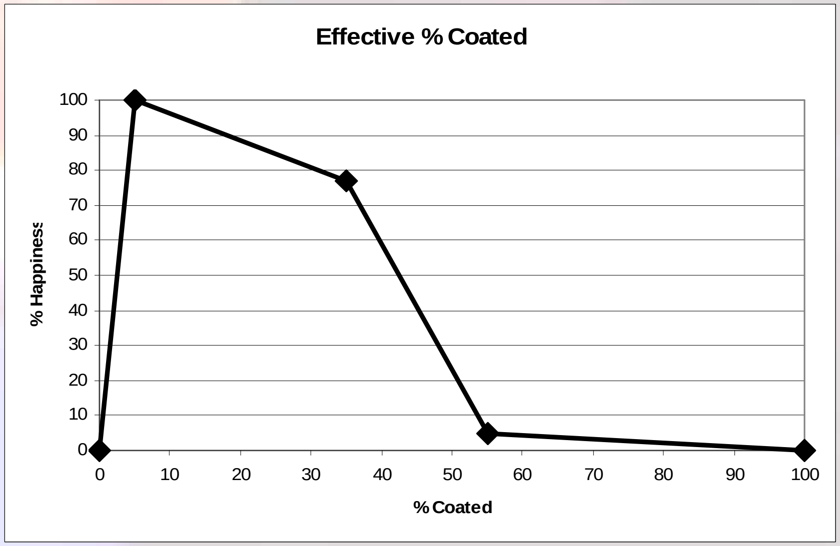
Flame Retardant Development





Flame Retardant Development





- Consumer happiness
  - Yields ranges (thresholds) for product comparison
  - Must be balanced with total cost to make product

Flame Retardant Development

- Consumer attributes
  - Retardancy time
  - Number of applications
  - Odor
  - Setting time
  - Effective amount
  - Biodegradability
  - Toxicity
- Measuring happiness
  - Assign happiness values to consumer attributes
  - Assign weights to attributes based on their relative importance

$$H_i = \sum_i w_i y_i$$

$$w_i = weight\ i^{th}\ component$$

$$y_i = happiness\ i^{th}\ component$$

$$\beta = \frac{H_2}{H_1}$$

Product Happiness

Consumer Attribute	Weight
Retardancy time	0.30
Thickness	0.15
Odor	0.15
Setting time	0.25
Effective amount	0.07
Biodegradability	0.04
Toxicity	0.04

Product Happiness

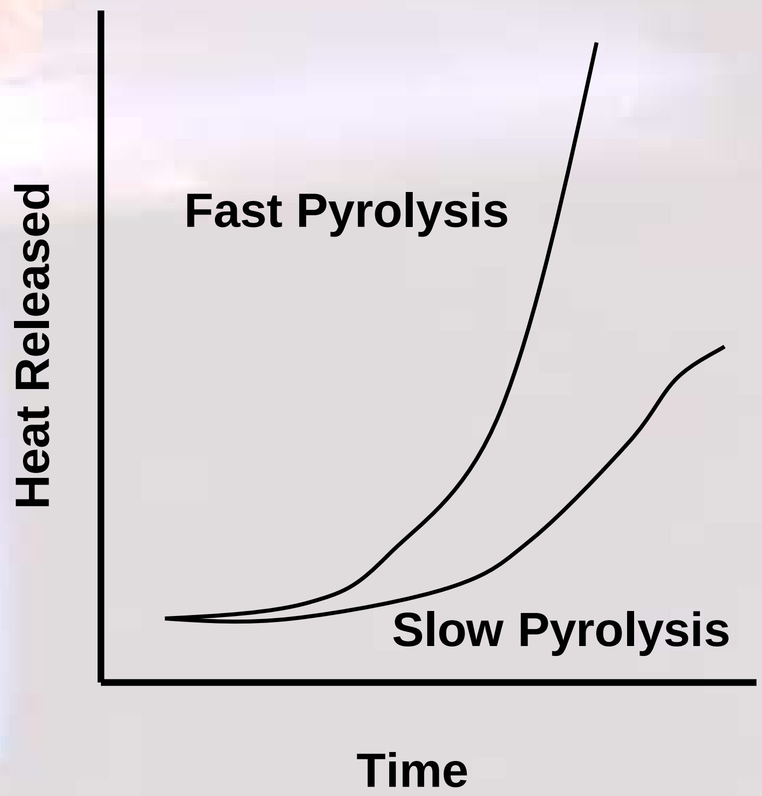
- Achieving Consumer Happiness
  - Relate product composition to physical models
    - % -- PVOH, Phosphate, Cloisite, and Water
  - Assume initial product composition
    - PVOH ~ 40%
    - Phosphate ~ 27%
    - Cloisite ~ 3%
    - Water ~30%
  - Vary compositions to achieve both a profitable product and a “happy” product

Product Happiness

- Modeling consumer happiness
  - Retardancy time
    - Altering the number of applications effects thickness (Basis 10cm X 10cm X 2cm)
    - Assume a basis “block” of treated wood (~3 coats @ ~ 1mm/coat)
  - Basic procedure
    - Polymer coating heats up with external heat source
    - Once a certain temperature is reached, polymer barrier degrades inducing char on wood
    - Char layer helps inhibit further heat transfer

Product Happiness

- Pyrolysis[6]
  - Fast pyrolysis
    - Wood flaming
    - Drastic Temperature increase
    - Evolution of combustible gasses
  - Slow pyrolysis
    - Wood glowing
    - Less exothermic
    - Fewer combustible gasses emitted
    - Enhanced through char formatoin



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[6] Browne, F.L. *Theories of the Combustion of Wood and Its Control. A Survey of the Literature. Forest Products Laboratory, Forest Service U.S. Department of Agriculture.*

Product Happiness

Char Formation[6]

$$X_i = \frac{m_{0,i} - m_i}{m_{0,i} - m_{char}}$$

***m_i*=Mass i^th component initially, (*0,i*), after heating, (*i*), (kg)**

***m_{char}*=Mass of char developed (kg)**

Char Layer Kinetics[6]

$$\frac{dX_i}{dt} = A_i e^{\left(\frac{-E_A}{RT_{avg}}\right)} \left(1 - X_i\right)^n$$

***A_i*=Frequency factor (min^{-1})**

***E_A*=Activation Energy (kJ/mol)**

***R*=Gas constant (kJ/mol-K)**

***T_{avg}*=Average wood temperature (K)**

n=Reaction order (unitless)

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[6] Browne, F.L. *Theories of the Combustion of Wood and Its Control. A Survey of the Literature. Forest Products Laboratory, Forest Service U.S. Department of Agriculture.*

Product Happiness

Char Layer Kinetics (cont'd)

$$\left(\frac{dX}{dt}\Big|_{T_{avg}}\right)_W = \left(\frac{dX}{dt}\Big|_{T_{avg}}\right)_C w_C + \left(\frac{dX}{dt}\Big|_{T_{avg}}\right)_L w_L + \left(\frac{dX}{dt}\Big|_{T_{avg}}\right)_H w_H$$

W_W=Wood as a whole

W_C =Cellulose component

W_L=Lignin component

W_H=Hemicellulose component

Product Happiness

- Modeling Consumer Happiness
  - Setting Time
    - Modeled diffusion of water based upon a varying number of applications
    - Use Gurney-Lurie tables[7] to estimate evaporation
      - Basis 10cm X 10cm X 2cm

$$n = \frac{x}{x_1} \qquad m = \frac{D_{AB}}{k_c x_1} \qquad Y = \frac{C_{As} - C_A}{C_{As} - C_{A0}} \qquad X = \frac{D_{AB} t}{x_1^2}$$

$$X = -0.392 \ln(Y) + 0.112$$

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[7]Welty, et al. *Fundamentals of Momentum, Heat & Mass Transfer.* 4th Edition. John Wiley & Sons, Inc 2001.

Product Happiness

- Modeling Consumer Happiness
  - Thickness
    - Relate number of coats by comparison with competitors to an average thickness (~1mm)
    - Determine resulting happiness
  - Odor
    - Assign different odor values to multiple functional groups
    - Relate these numeric values to consumer preferences

F.G.	Hydrocar-bons	Alcohols/ halogens	Carboxylic Acids	Ethers	Aromatics	Amines	Ketones	Mercaptans
#	0	1	2	3	4	5	6	7

Product Happiness

- Modeling Consumer Happiness
  - Effective Amount
    - Assumed thickness
    - Determine the effective amount (maximum allowable volume percentage ~ 35% by volume)
  - Biodegradablilty
    - If product is biodegradable assign 1, if not assign 0
  - Toxicity
    - If product is toxic assign 0, if not assign 1
- Determining Product Happiness
  - Solve for compositions that provide greatest profit
  - Solve for compositions that provide greatest happiness

Product Happiness

- Our Product – “Freeze Flame Nano”
  - PVOH = 50%
  - Phosphate = 15%
  - Cloisite = 3%
  - Water = 32%
- Happiest Product
  - PVOH = 50%
  - Phosphate = 27%
  - Cloisite = 3%
  - Water = 20%

Product Happiness

- Our major competitor
  - Firetect WT-102
    - 18.4% Polyvinylidene Chlorine
    - 21.8% Phosphate
    - 3.4% Sodium Salt
    - 41.9% Butyl Acetate

Product Happiness

- Resulting Happiness
  - By varying compositions to provide the most profitable product

H_1=0.868 ***H_2=0.574***

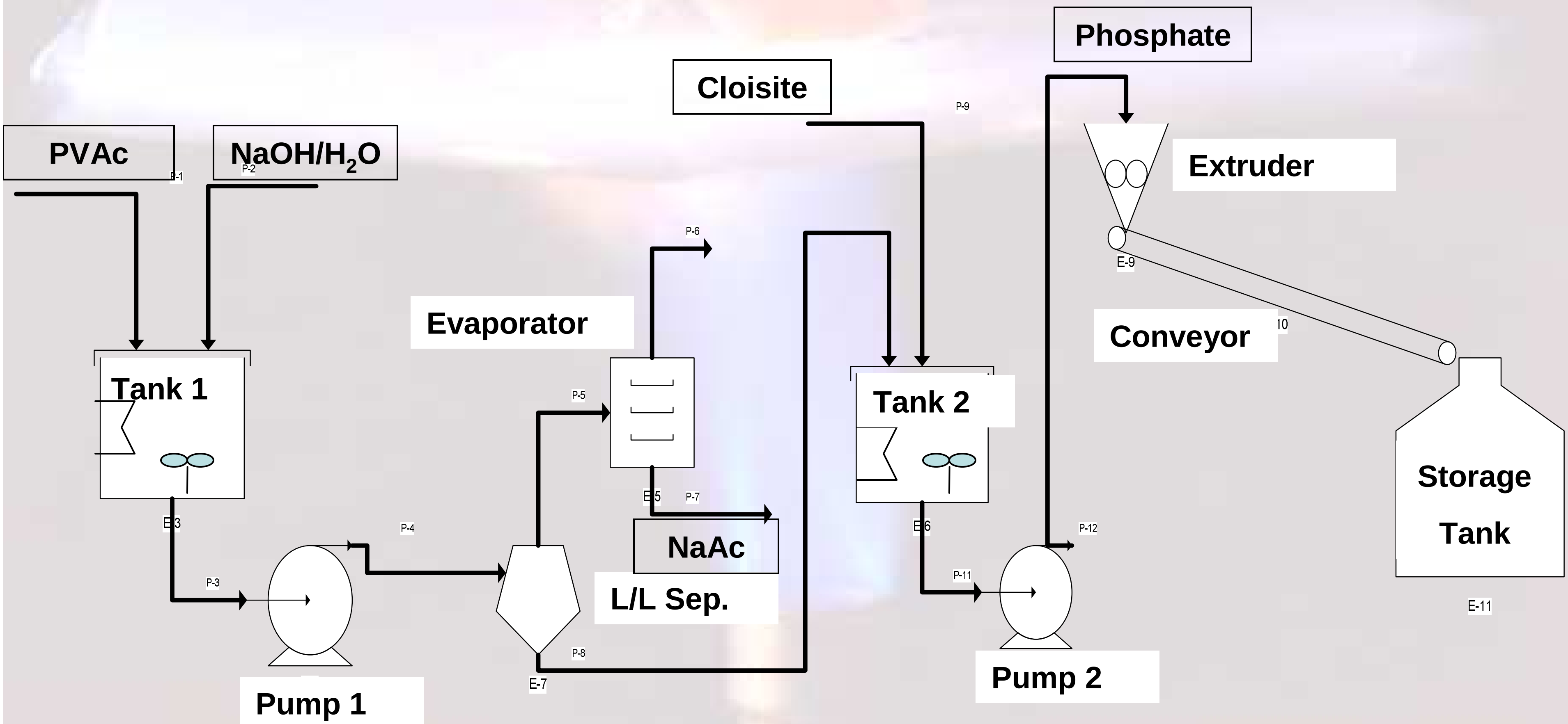
$$\beta = \frac{H_2}{H_1} = 0.661$$

- Resulting Happiness
  - By varying compositions to provide the happiest product

H_1=0.930 ***H_2=0.574***

$$\beta = \frac{H_2}{H_1} = 0.617$$

Process Flow Diagram



Demand

- Equations used to determine demand

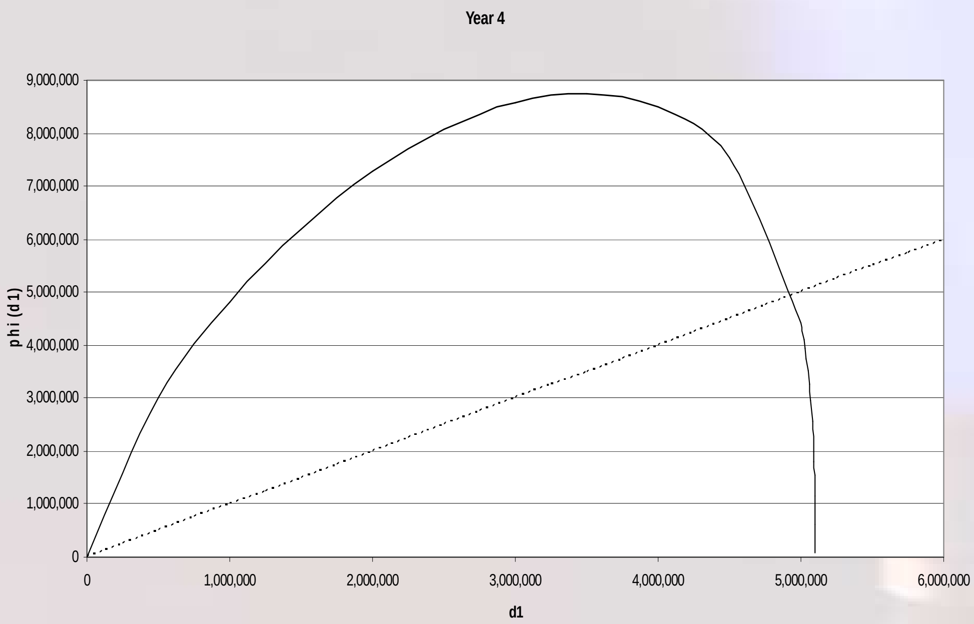
  - $$\beta p_1 d_1 = \alpha p_2 d_2 \left(\frac{d_1{}^{\alpha}}{d_2{}^{\beta}} \right)$$

  - $$Y = p_1 d_1 + p_2 d_2$$

  - Solving both equations for d_2 and setting them equal to each other will give our demand

Demand

$$d_1 = d_1^{\alpha}\left(\frac{\alpha}{\beta}\right)\left(\frac{p_2}{p_1}\right)\left(\frac{Y}{p_2} - \frac{p_1 d_1}{p_2}\right)^{1-\beta}$$



Year	Demand (lb/year)
1	19,000
2	930,000
3	**3,900,000**
4	4,900,000
5	5,300,000
6	**5,500,000**
7	5,800,000
8	6,000,000
9	6,300,000
10	**6,700,000**

Regret Analysis

NPW			
	Low	Med	High
Design 1	$ 3,600,000	$ (1,300,000)	$ (6,100,000)
Design 2	$19,000,000	$13,000,000	$ 6,000,000
Design 3	$22,000,000	$15,000,000	$ 9,000,000
Max	$22,000,000	$15,000,000	$ 9,000,000

Regret Analysis

Regret				
	Low	Med	High	Max Regret
Design 1	18,400,000	16,300,000	15,100,000	18,400,000
Design 2	3,000,000	2,000,000	3,000,000	3,000,000
Design 3	0	0	0	0
			Minimax	0

Process Capacity

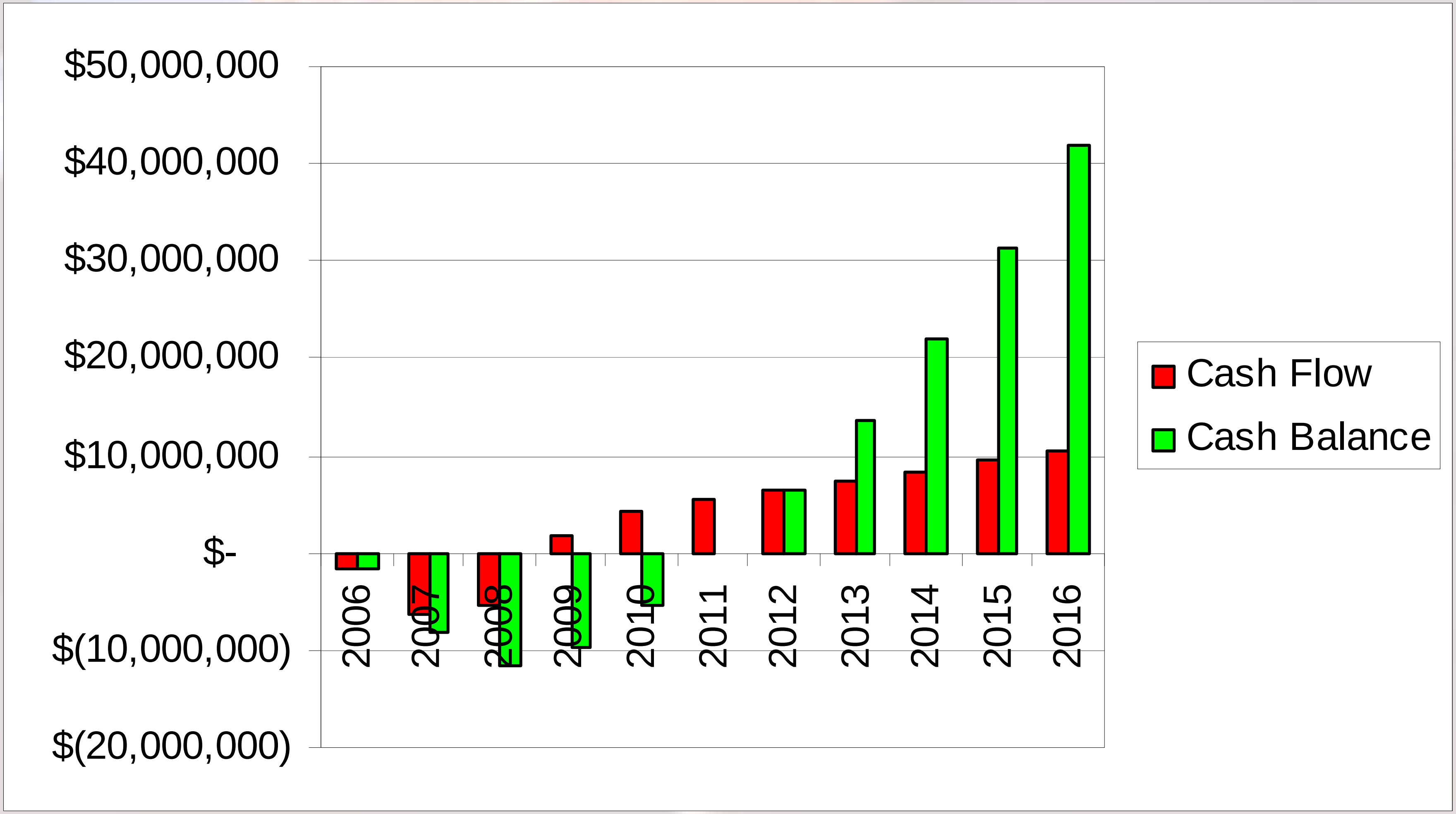
Component	Capacity
Tank 1	7.2 m^3
Tank 2	4.1 m^3
Pump 1	4.9 kW
Pump 2	0.6 kW
Settler	6.8 m^3
Evaporator	3.2 m^3
Extruder	0.7 m^3
Storage	85 m^3

Equipment Cost

Tank 1	$40,000
Tank 2	$25,000
Pump 1	$7,000
Pump 2	$5,000
Settler	$76,000
Dryer	$25,000
Heater 1	$16,000

Heater 2	$6,000
Extruder	$47,000
Conveyor	$18,000
Storage	$40,000
Piping	$5,000
Total Cost	**$310,000**

Economics


$50,000,000
$40,000,000
$30,000,000
$20,000,000
$10,000,000
$-
$(10,000,000)
$(20,000,000)
2006
2007
2008
2009
2010
2011
2012
2013
2014
2015
2016
Cash Flow
Cash Balance

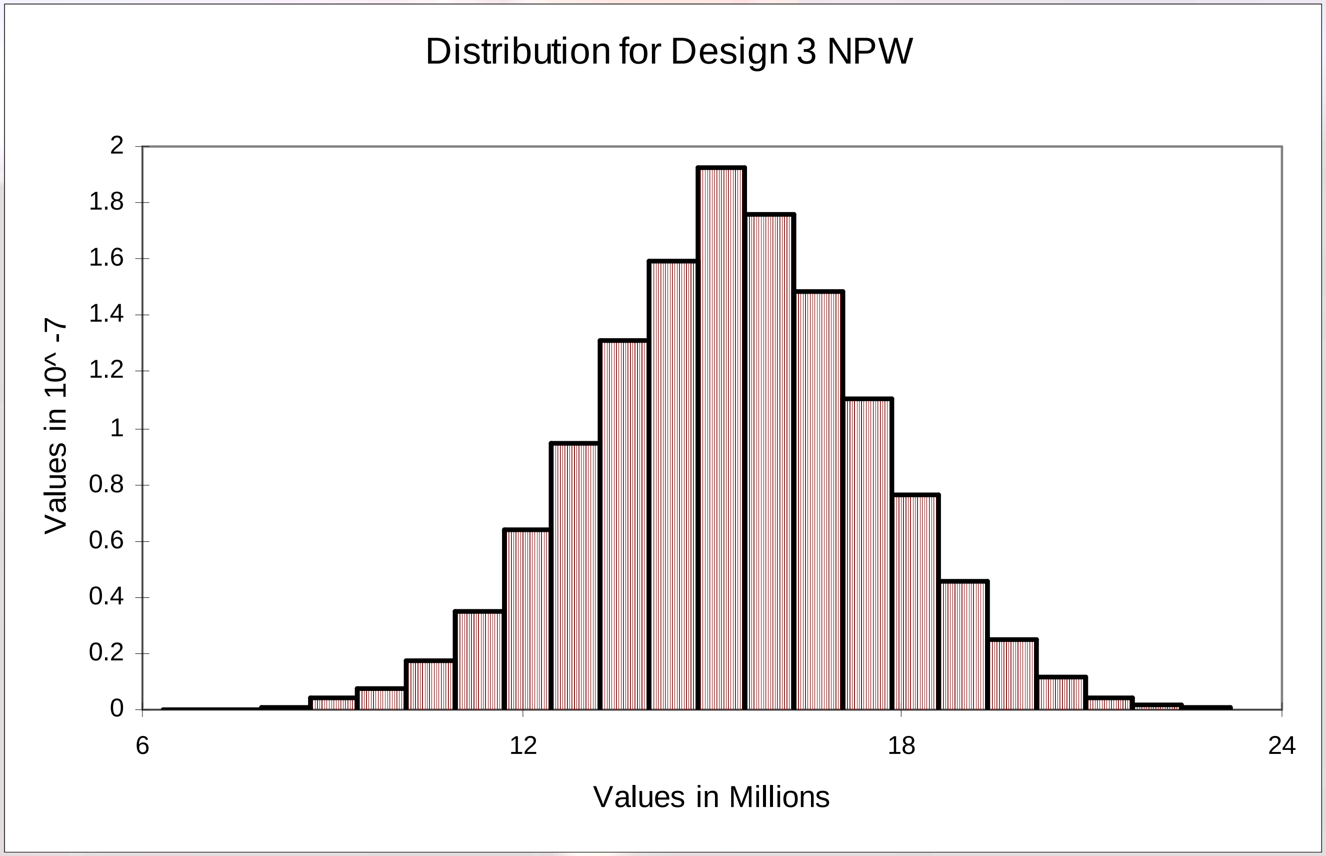
Economics

$$NPW = \sum_{n=1}^{10} \frac{CF_n}{(1+i)^n} + \frac{WC+SV}{(1+i)^{10}} - TCI$$

- TCI = $1,700,000
- NPW = $15,300,000

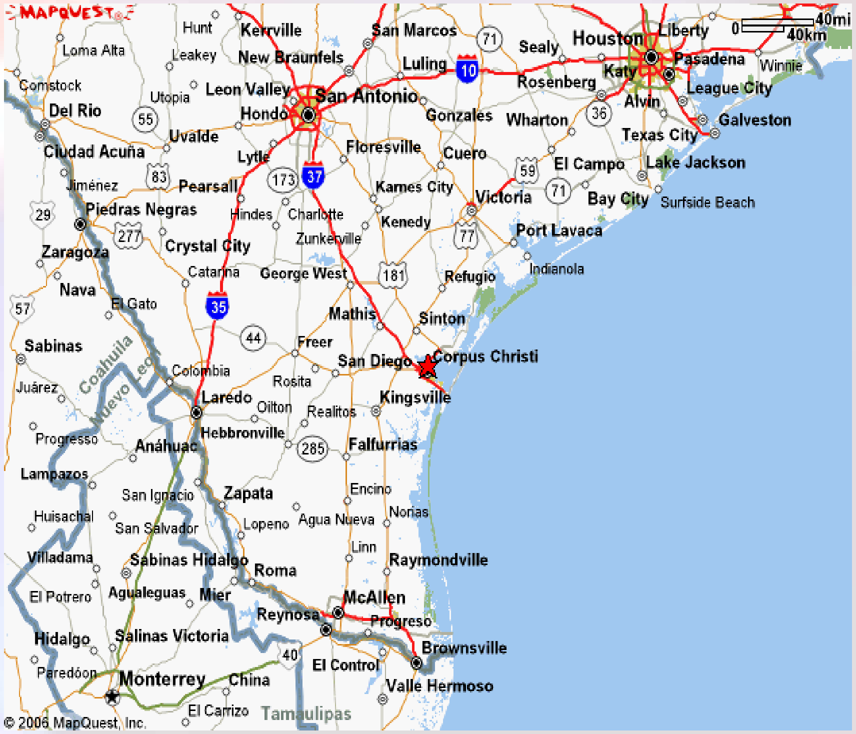
[8]West, et al. *Plant Design and Economics for Chemical Engineers.* 5th Edition. McGraw-Hill 2004.

Risk Analysis



Plant Location / Distribution

- Corpus Christi, TX
  - Supply
    - Phosphate - Humble, TX
    - Cloisite - Gonzales, TX
    - Polymer - La Porte, TX
  - Demand
    - Large construction markets in Houston, Dallas, Kansas City



Target Consumers

- Turner Construction Company
  - Houston, Dallas, Kansas City
- Hansel Phelps Construction Co.
  - Austin
- JE Dunn Construction Company
  - Dallas, Houston, Fort Worth, Kansas City
- Centex Construction
  - Dallas, Houston, Plano, Oklahoma City

Conclusions

- Freeze Flame Nano is durable, heat resistant, char-inducing flame retardant
- It will bind to various surfaces because of its polar nature
- We feel the construction industry would benefit most from FFN

Recommendations

- Find a cheaper source of PVA
- Research cheaper alternatives (polymers)
- Perform rigorous lab-scale tests on FFN to determine quantitative performance
- Vary color of product

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Questions?